

polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ^{13}C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

Conversions of Liquefaction

The structures of low-rank coals are characterized by smaller aromatic ring clusters joined by a higher proportion of weak crosslinks than coals of higher rank. This kind of structural feature results in their thermally sensitive natures. The bond cleavages of those weak crosslinks may occur at low temperatures to yield free radicals. If the radicals are not stabilized, retrogressive reactions producing materials difficult to liquefy will take place. Therefore, it is important to determine the optimum temperatures for each coal at which thermal cleavages readily occur while retrogressive reactions are unlikely to occur. Liquefaction experiments were carried out at 250°C, 300°C, 350°C, 400°C and 450°C with the presence of H_2 and the absence of a catalyst and a solvent. The conversion data are shown in Figure 1. At 350°C and below, reactions of all three coals are very limited, with conversions below 20%. As temperature increases to 400°C and 450°C, conversions significantly and continuously increase. However, our earlier study [8] has shown that although a temperature of 450°C seems to be more beneficial in obtaining high conversions, it causes severe retrogressive reactions which are indicated by very high aromaticities of the reaction residues. Therefore 400°C is considered to be the best temperature for liquefaction of these coals.

However, even at the optimum temperature, 400°C, no more than 50% of the coals can be converted to THF solubles when neither a catalyst nor a solvent is involved. In an effort to enhance the conversions, ATTM was added as a catalyst precursor; tetralin and 1-methylnaphthalene were used as a hydrogen donor and a non-donor solvent respectively. The effects of the catalyst and solvents are presented in Figure 2. By using the catalyst, the conversions were increased from 45% to 95.5% for the DECS-1 coal, from 24.2% to 78.5% for the DECS-9 coal, and from 30.6% to 63.5% for the DECS-11 coal. These increases are contributed by significant gains in oils and asphaltenes. The gas yields in the catalytic and non-catalytic reactions are very similar for each coal, which is in an agreement with our earlier observation that the gas yield is a function of temperature, and the use of the catalyst or the donor solvent has no significant effect on it [8]. To maximize the conversion, tetralin and 1-MN were applied in addition to the catalyst. As a donor solvent, tetralin further causes more coal converted to THF solubles for DECS-9 and DECS-11. For DECS-1, there is no increase in conversion, although that is because even with only the catalyst, the conversion reaches 95%. It is reasonable to say that this may already be the practical maximum conversion limit. As a non-donor solvent, 1-MN has a very insignificant effect on the conversions of all the three coals. Comparing conversions at different reaction conditions, it is found that adding the catalyst is sufficient to achieve the highest conversion for the DECS-1 coal; while it is necessary to add both the catalyst and the donor solvent for the DECS-9 and the DECS-11 coals. Among these coals, the DECS-11 is relatively unreactive, its conversion can reach only about 80% at the best reaction condition applied in this study.

Product Characterization

To produce materials from a coal for making the special chemicals, a high conversion has to be achieved and, more importantly, those desirable structural units in the coal macromolecular network have to be converted to individual molecules. In this work, one- to four-ring aromatic or alkylaromatic compounds were desired. In other words, more aromatic carbons have to be converted to THF solubles. To determine the amounts of aromatic carbons converted, the reaction residues as well as the vacuum-dried coal samples were analyzed by CPMAS ^{13}C NMR. The spectra were curve-fitted and integrated, and the aromaticities (f_a) were calculated based on the areas covered by the spectra in aromatic and aliphatic regions. Since the weights of both coals and residues are known, and data of overall conversions from coals to THF solubles are available, the percentages of the reacted aliphatic and aromatic carbons can be determined, as shown in Figure 3 and 4. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed, while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the least. In Figure 4, the aromatic carbons appear to be more difficult to be removed from the coal networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with. This indicates the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the

polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ^{13}C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

Conversions of Liquefaction

The structures of low-rank coals are characterized by smaller aromatic ring clusters joined by a higher proportion of weak crosslinks than coals of higher rank. This kind of structural feature results in their thermally sensitive natures. The bond cleavages of those weak crosslinks may occur at low temperatures to yield free radicals. If the radicals are not stabilized, retrogressive reactions producing materials difficult to liquefy will take place. Therefore, it is important to determine the optimum temperatures for each coal at which thermal cleavages readily occur while retrogressive reactions are unlikely to occur. Liquefaction experiments were carried out at 250°C, 300°C, 350°C, 400°C and 450°C with the presence of H_2 and the absence of a catalyst and a solvent. The conversion data are shown in Figure 1. At 350°C and below, reactions of all three coals are very limited, with conversions below 20%. As temperature increases to 400°C and 450°C, conversions significantly and continuously increase. However, our earlier study [8] has shown that although a temperature of 450°C seems to be more beneficial in obtaining high conversions, it causes severe retrogressive reactions which are indicated by very high aromaticities of the reaction residues. Therefore 400°C is considered to be the best temperature for liquefaction of these coals.

However, even at the optimum temperature, 400°C, no more than 50% of the coals can be converted to THF solubles when neither a catalyst nor a solvent is involved. In an effort to enhance the conversions, ATTM was added as a catalyst precursor; tetralin and 1-methylnaphthalene were used as a hydrogen donor and a non-donor solvent respectively. The effects of the catalyst and solvents are presented in Figure 2. By using the catalyst, the conversions were increased from 45% to 95.5% for the DECS-1 coal, from 24.2% to 78.5% for the DECS-9 coal, and from 30.6% to 63.5% for the DECS-11 coal. These increases are contributed by significant gains in oils and asphaltenes. The gas yields in the catalytic and non-catalytic reactions are very similar for each coal, which is in an agreement with our earlier observation that the gas yield is a function of temperature, and the use of the catalyst or the donor solvent has no significant effect on it [8]. To maximize the conversion, tetralin and 1-MN were applied in addition to the catalyst. As a donor solvent, tetralin further causes more coal converted to THF solubles for DECS-9 and DECS-11. For DECS-1, there is no increase in conversion, although that is because even with only the catalyst, the conversion reaches 95%. It is reasonable to say that this may already be the practical maximum conversion limit. As a non-donor solvent, 1-MN has a very insignificant effect on the conversions of all the three coals. Comparing conversions at different reaction conditions, it is found that adding the catalyst is sufficient to achieve the highest conversion for the DECS-1 coal; while it is necessary to add both the catalyst and the donor solvent for the DECS-9 and the DECS-11 coals. Among these coals, the DECS-11 is relatively unreactive, its conversion can reach only about 80% at the best reaction condition applied in this study.

Product Characterization

To produce materials from a coal for making the special chemicals, a high conversion has to be achieved and, more importantly, those desirable structural units in the coal macromolecular network have to be converted to individual molecules. In this work, one- to four-ring aromatic or alkylaromatic compounds were desired. In other words, more aromatic carbons have to be converted to THF solubles. To determine the amounts of aromatic carbons converted, the reaction residues as well as the vacuum-dried coal samples were analyzed by CPMAS ^{13}C NMR. The spectra were curve-fitted and integrated, and the aromaticities (f_a) were calculated based on the areas covered by the spectra in aromatic and aliphatic regions. Since the weights of both coals and residues are known, and data of overall conversions from coals to THF solubles are available, the percentages of the reacted aliphatic and aromatic carbons can be determined, as shown in Figure 3 and 4. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed, while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the least. In Figure 4, the aromatic carbons appear to be more difficult to be removed from the coal networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with. This indicates the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the

DECS-1 coal, the catalyst is sufficient to achieve over 95% aromatic conversion; for the DECS-9 coal, with both the catalyst and the donor solvent, 98% can be obtained; while for the DECS-11 coal, the least convertible coal in terms of conversion, even with both the catalyst and the donor solvent, only about 70% aromatic conversion can be achieved.

The asphaltenes and the preasphaltenes were also studied by CPMAS ^{13}C NMR. Unfortunately, their spectra look so much like the vacuum-dried coals that they can not be characterized without other analytical techniques. The hexane solubles, defined as oils, were analyzed by gas chromatography, identified by gas chromatography/mass spectrometry. Figure 5 represents the oils from the DECS-9 coal without the catalyst or the donor solvent, *a*; with the catalyst but not the donor solvent, *b*; and with both the catalyst and the donor solvent, *c*. In Figure 5-*a*, the oil contains a high proportion of long-chain alkanes, i. e. from $n\text{-C}_{12}$ to $n\text{-C}_{33}$. At retention time of about 6.0 minutes, there is a very strong peak identified as toluene. In low-rank coals such as DECS-9, small aromatic clusters dominate [4, 5], and they are connected by aliphatic crosslinks. Once the crosslinks break, these small aromatic clusters will be released. In the DECS-9, as shown in our recent work [4], one-ring structural units are abundant and thus when liquefying the coal, toluene (instead of benzene) will be a major product, because the benzylic C-C bond has a much lower dissociation energy than the phenyl C-C bond [9]. Relative to those of aliphatics, the amounts of aromatic compounds in the oil (with relation times from 15 minutes to 30 minutes) are much smaller (Figure 5*a*), indicating that this reaction condition suppresses the production of aromatic compounds in the oil. Comparing with the case without the catalyst or the donor solvent, adding ATTM into the reaction system appears to favor the yields of aromatic compounds. As shown in Figure 5*b*, the alkylbenzenes, phenol and alkylphenols are the major components in the oil. This observation agrees with our earlier finding that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons [8]. Furthermore, when we use tetralin in addition to the catalyst, the yields of phenolic compounds remain very high, Figure 5*c*; the one-ring aromatics seem to be in a lower proportion; and the yields of two-ring aromatics, such as indane, alkylindanes and alkyl-naphthalenes have increased. The large peaks at retention times about 24.5 minutes and 27.0 minutes are due to tetralin and naphthalene, the solvent and the dehydrogenated solvent. It is likely that the increased yields of alkylindanes and alkyl-naphthalenes are due, at least in part, to the use of tetralin. In the GC study, three- or four-ring compounds appear to be in small amounts and not affected by either the catalyst nor the solvent. This may be because they are less abundant than the one- or two-rings in the coal, or because their solubilities in hexane are smaller and therefore it is hard to detect the differences at different cases.

CONCLUSIONS

In liquefaction of the three low-rank coals, temperature is found to be optimum at 400°C. Reactions without the catalyst or the donor solvent provide very low conversion, i. e. less than 50%, for all three coals. As for the DECS-1 coal, the ATTM-derived catalyst is sufficient in terms of a high conversion. As for the DECS-9 coal, only when both the catalyst and the donor solvent are used can conversion as high as 98% be achieved. For the DECS-11 coal, even under the best reaction condition, which is at 400°C with the catalyst and the solvent, the conversion only reaches 78%. Therefore, the DECS-11 coal is the least convertible coal among the three.

The investigation on reaction residues by solid-state NMR shows that it is relatively easier to convert aliphatic carbons from coals to THF solubles, and that the catalyst and the donor solvent can both be beneficial but the effects are moderate. The amounts of aromatic carbons being converted from the coals appear to be small when the catalyst or the donor solvent is not present, and they can even be negative, indicating that retrogressive reactions have occurred. Adding the catalyst and the solvent significantly enhances the reactions of aromatic carbons.

The study of the oils agrees with what has been observed on the residues. Without the presence of the catalyst or the solvent, the oils contain large amounts of long-chain alkanes; while with the catalyst and the donor solvent, more aromatic materials, such as phenolic compounds, alkylbenzenes and some two-ring compounds, can be produced. With further extraction and purification, these compounds might be used as for making specialty chemicals for some advanced materials.

ACKNOWLEDGEMENT

The authors gratefully thank the United States Department of Energy for the financial support. We also want to thank Dr. M. Baird and Dr. M. A. Nowak for helpful discussions.

REFERENCES

1. Song, C., and Schobert, H. H., *ACS Div. of Fuel Chem. Prepr.* 1992, **37**(2), 524-532
2. Song, C., and Schobert, H. H., *Fuel Proc. Tech.*, 1993, **34**, 157-196

- Schlosberg, R. H., Chemicals from coal, in *Fuel Science and Technology Handbook*, Ed. by J. G. Speight., 1990, Chap 24, Marcel Dekker
- Song, C., Hou, L., Saini, A. K., Hatcher, P. G., and Schobert, H. H., *Fuel Proc. Tech.*, 1993, 34, 249-276
- Schobert, H. H., *Resources, Conservation and Recycling*, 1990, 3, 111-123
- Schobert, H. H., *The Chemistry of Hydrocarbon Fuels*, 1990, Butterworth
- Huang, L., Song, C., and Schobert, H. H., *ACS Div. of Fuel Chem. Prepr.* 1992, 37(1), 223-227
- Huang, L., Song, C., Schobert, H. H., *ACS Div. of Fuel Chem. Prepr.* 1993, 38(3), 1093-1099
- McMurry, J. *Organic Chemistry*, 1984, Brooks/Cole

Table 1. Analysis of the coal samples

	DECS-1	DECS-11	DECS-9
Sources & Rank			
state	Texas	North Dakota	Montana
county	Freestone	Mercer	Bighorn
city	Fairfield		Decker
seam	Bottom	Beulah	Dietz
ASTM rank	subbit C	lignite	subbit B
sampling date	12/11/89	6/15/93	6/12/90
Proximate (wt%, ar)			
moisture	30.0	33.4	24.7
ash	11.1	6.4	4.8
volatile	33.2	37.4	33.5
fixed carbon	25.8	22.9	37.1
Elemental (wt%, dmmf)			
carbon	76.1	74.2	76.1
hydrogen	5.5	4.4	5.1
nitrogen	1.5	1.0	0.9
organic sulfur	1.1	0.4	0.3
oxygen	15.8	20.0	17.5

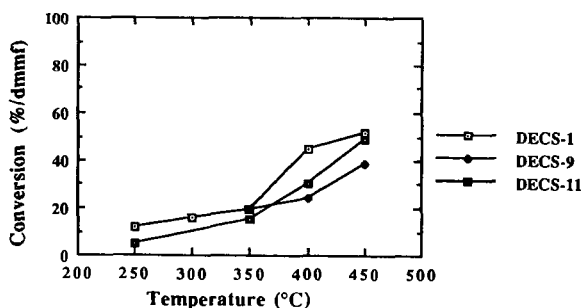


Figure 1. Conversions of the three coals at temperatures from 250°C to 450°C without a catalyst or a solvent

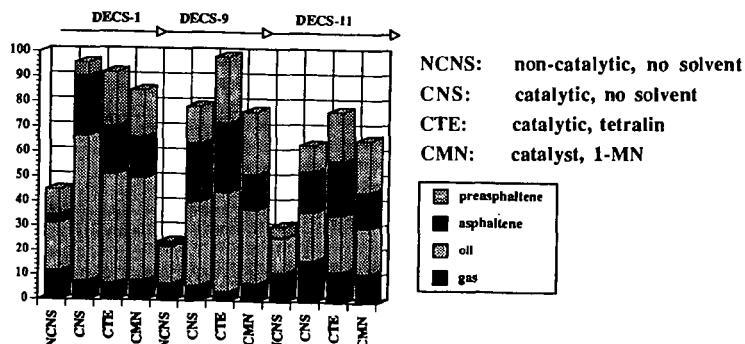


Figure 2. Liquefaction conversions of the three coals at 400°C under four different reaction conditions

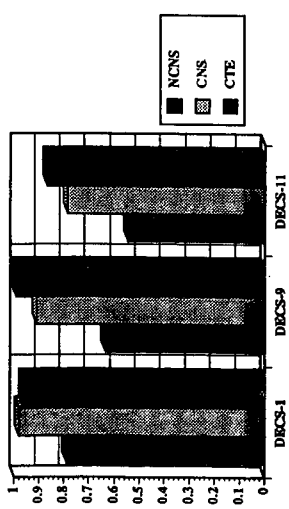


Figure 3. The amounts of aliphatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

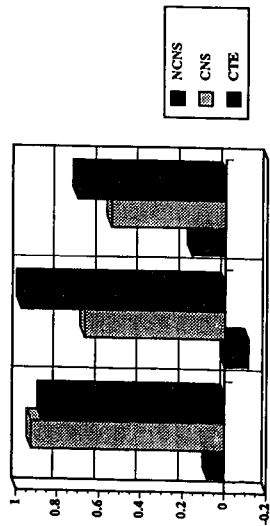


Figure 4. The amounts of aromatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

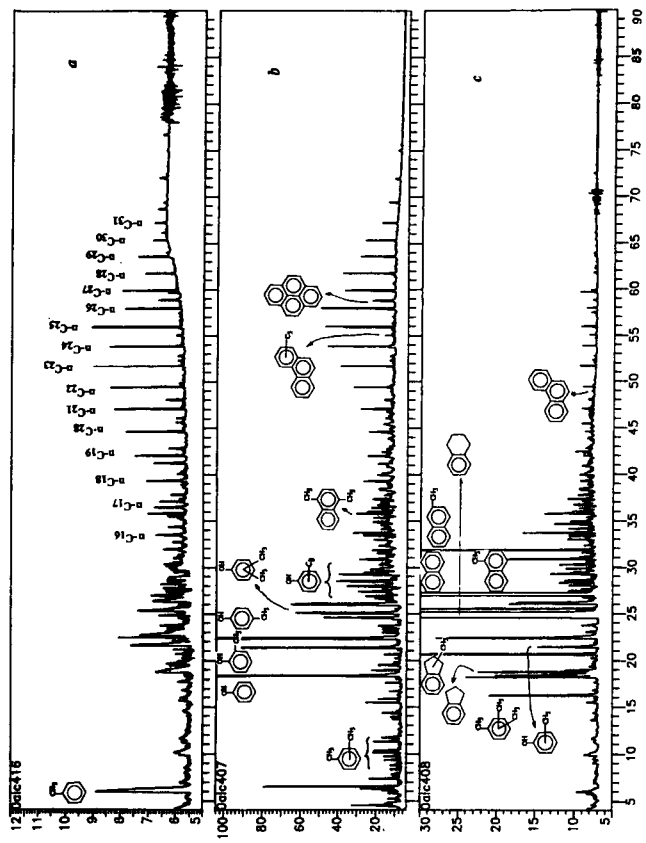


Figure 5. Analysis of the oil samples from the DECS-9 coal using gas chromatograph. a) the sample from the reaction without a catalyst or a solvent; b) the sample from the reaction with the ATTM-derived catalyst but without a solvent; c) the sample from the reaction with both the catalyst and tetralin.

PRODUCTION OF ACTIVATED CARBONS FROM A VITRAIN CONCENTRATE FROM THE STOCKTON COAL.

Chris Toles, Susan M. Rimmer (Department of Geosciences, University of Kentucky, Lexington, KY 40506-0053)

Frank Derbyshire, and Marit Jagtøyen (Center for Applied Energy Research, University of Kentucky, 3572 Iron Works Pike, Lexington, KY 40511)

Keywords: Activated carbon, chemical activation, phosphoric acid

Introduction

Earlier, related studies have shown that porous carbons can be produced by phosphoric acid activation of coals and hardwood [1-4]. One of the findings was that the development of surface area appears to be rank-dependant. It is also supposed that maceral composition will affect the response to phosphoric acid activation, although there is no available information on this subject.

In this context, a study has been initiated of the phosphoric acid activation of coal macerals. The objectives are to examine the effects of maceral composition and rank on porosity development, and to understand the individual and collective contributions of maceral groups to the activation of coals by phosphoric acid.

In this study, a vitrinite concentrate from an hvA bituminous coal (Stockton) was used as starting material for the production of activated carbons by H_3PO_4 activation. The chemical, morphological, and surface area changes were followed as a function of reaction temperatures and are compared to the results of previous studies.

Experimental

Maceral Separation

Bench samples of Stockton coal (hvA bituminous) were collected from fresh highwall exposures in the field in eastern Kentucky. Samples were chosen for their high vitrain content. In the laboratory, vitrain-rich benches were chosen to facilitate hand picking of vitrains. The samples were coarsely ground in a mortar and pestle to about 4 mesh and then split into approximately 10g samples for later experiments.

Petrographic pellets were made from a representative split of the vitrain concentrate to ascertain maceral content and purity. Standard preparation and polishing techniques were used. The Stockton sample was found to have a mineral matter-free vitrinite content of 93.5%. Table 1 shows maceral composition for this sample as determined by point-count analysis.

Carbon Synthesis

Activated carbons were produced according to procedures described in earlier carbon studies [1-4]. A split of the vitrinite concentrate was placed in a quartz crucible with a known volume and concentration of phosphoric acid to give an acid/dry coal ratio of approximately 0.96. The quartz boat was placed in a stainless steel oven tube, which was then flushed with nitrogen gas. It was then reacted at a low temperature (170°C) for 0.5h after which it was heated to a final heat treatment-temperature (HTT) ranging from 350°C to 550°C, and allowed to react for 1h at temperature. After the sample had cooled to room temperature it was leached with hot distilled water until the pH of the leachate was at or near neutral. Leached samples were then dried in a convection oven at about 100°C for 1.5 to 2h. Prior to nitrogen BET analysis, these samples were further dried in a vacuum oven at 110°C to insure complete outgassing. For comparison thermal counterparts were also run. These splits were treated as already described except that no acid was added prior to heat treatment.

Characterization

Proximate and ultimate analyses were performed following standard procedures. Fourier-transform infrared spectroscopy (FTIR) data were collected on a Nicolet 20SX spectrometer at 4 cm^{-1} resolution using pressed KBr pellets which contained approximately 0.5wt % sample. Spectra were normalized to a 1/200 concentration of sample/KBr to allow direct comparison between spectra.

Epoxy impregnated pellets of each activated carbon were prepared for petrographic and vitrinite reflectance analysis. Optical characterization was performed on a Zeiss microscope equipped with a 40x oil immersion lens. Modal maximum vitrinite reflectance ($\%R_{\text{max}}$) measurements were collected from 25 samples/pellet. Measurements were taken at 546nm wavelength and standardized against a set of glass standards. Photographs were taken of several of the fields of view using the same microscope equipped with a 40x Antiflex lens. In several instances, the polars were crossed to determine the extent of anisotropy in the carbons.

Surface area measurements were obtained from nitrogen adsorption isotherms at 77K using a Quantachrome Autosorb 6. Macro and meso-pore volumes and surface areas were measured using a Quantachrome Autoscan-60 mercury porosimeter.

Results and Discussion

Optical Characteristics

The maximum vitrinite reflectance of the vitrinite-rich samples heat treated in the presence and absence of acid increases with increasing HTT (Fig. 1). As found in earlier studies, up to HTT of 450°C the acid-treated carbons exhibit higher vitrinite reflectances than their thermal analogs, while above 450°C this relationship is reversed. Vitrinite rich samples follow the same trends that were observed for whole coals [1-4].

In most of the carbons, it was noted that the desmocollinite reflectance was slightly lower than that of telocollinite, throughout the range of activation temperatures.

Reflectance data reported here were measured on telocollinite. The apparent difference in reflectance between the two submacerals lessened with increasing HTT. At HTTs above 350°C it became more difficult to differentiate between desmocollinite and telocollinite, and this, as well as misidentification of semifusinite, may account for the spread in vitrinite reflectance values that were found in taking measurements. Resinite occurs in the desmocollinite of the vitrinite-rich samples up to HTTs of 350°C, after which it was no longer evident, having been either transformed or removed.

Some degree of anisotropy was observed in the vitrinites at higher HTTs, changes in reflectance of up to 0.1% were noted upon rotation of the stage. This anisotropy was clearly visible when the antillex lens was used. The anisotropy did not develop to a great extent even at 450°C or 550°C, rather it occurred around vacuoles in the vitrinites.

These vacuoles (approximately 50 μm in diameter) were formed in both the thermal and acid-treated samples and become far more prevalent with increasing HTT. In the acid-treated samples at HTT of 350°C, some of the larger pieces of vitrinite showed evidence of a reaction front, usually associated with some of the vacuoles as well as with cracked edges. There was a visible difference in reflectance of the vitrinite by as much as 0.3% across these aureoles, with the higher reflectances being in the outer region. Examination of these aureoles with the antillex objective suggested that they were reaction fronts rather than anisotropic zones. At the maximum HTT (550°C) the acid treated samples appeared much more macerated and friable, exhibiting many small pits between the larger vacuoles.

Chemical composition

Both the acid-treated and thermal suites of samples show a loss of hydrogen with increased HTT (Fig. 2); however, the loss of hydrogen with HTT is more extensive upon reaction with H_3PO_4 . This result supports the FTIR observation that the acid treated samples lost aliphatic hydrogen more quickly than the thermal samples as found in previous studies with whole coals [1-4]. A negative relationship is found to exist between % R_{max} and H/C ratio. As the samples in both suites lose hydrogen there is a corresponding increase in % R_{max} (Fig. 1).

FTIR analyses show good correspondence with the elemental data with respect to loss of hydrogen. As can be seen in Figure 3, the overall trend of decreasing aliphatic content with increased HTT can be seen by the disappearance of peaks in the 2900 cm^{-1} wavenumber range. The existence of various inorganic phases present in these samples obscures many of the peaks in the lower wavenumber range.

In the acid-treated samples there is a very strong peak around 1200 cm^{-1} that in previous studies has been assigned to phosphate esters [3-4]. In these samples it appears that there is significant overlap in this region with inorganics that appear in the thermal control samples as a peak only slightly shifted up from the 1200 cm^{-1} peak.

The carbonyl peak at 1700 cm^{-1} decreases in intensity and shifts to lower wavenumbers with increasing HTT in both the thermal and acid-treated samples. It disappears completely above 350°C. This shift is greater in the thermal blanks, between the parent and 350°C, than in the acid-treated samples. This may indicate that the carbonyl functions in the acid-treated samples are more strongly bound, perhaps by resonance with nearby double bonds.

Aliphatic peaks at about 2900 cm^{-1} decrease in both of the sample suites and are virtually eliminated above 350°C. These peaks decrease more quickly for the acid-treated samples than for the thermal samples, and the aromatic C-H peak at 3000 cm^{-1} appears more well developed in the acid runs. This latter effect may be more a function of greater intensity of the -OH broad peak which may be overlapping this peak in the thermal runs.

Surface Area Measurements

Table 2 shows that the thermally treated vitrain samples develop virtually no porosity or surface area. Upon acid treatment, porosity starts to develop after 350°C, with most of the porosity residing in the microporous range.

The data on the development of surface areas of acid treated samples with HTT are shown in figure (4) which also shows results obtained by Jagtoyen et al. [6] for different starting materials. In each case there is a maximum in the surface area with HTT which decreases with rank and shifts to higher temperatures.

The extent of surface area development decreases in the order: hardwood > subbituminous coal > hvC bituminous coal > hvA vitrain, which tends to confirm the supposition that the extent of metamorphism reduces the response to phosphoric acid activation [6].

Conclusions

A study has been made of the chemical activation of a vitrain concentrate, hand-picked from the Stockton hvA bituminous coal. Reactions were conducted at HTT from 350°C to 550°C. Thermal blanks were generated under similar conditions for comparison.

Changes in chemical composition were followed by elemental analysis and FTIR. With increasing HTT, acid-treatment promotes more extensive loss of hydrogen. The infrared spectra show the early loss of aliphatic groups and increasing aromaticity for samples reacted with H₃PO₄. Shifting behaviour of the carbonyl peak at 1700cm⁻¹ in the spectra suggests greater resonance stabilization of carbonyl functions in the acid-treated samples than in the thermal control samples.

Corresponding to these chemical changes, there is an increasing maximum vitrinite reflectance with HTT: this is higher for acid-treated than thermal carbons up to about 450°C, above which temperature the reverse is the case. These changes are in keeping with the findings of earlier studies.

Surface area development with HTT is less than found for lower rank materials, which is also in keeping with the suggestion that metamorphic changes reduce the response to H₃PO₄ activation. Hence, at this stage of the research, it is not yet possible to distinguish maceral from rank effects on pore structure development.

Acknowledgments

This study was made possible with the assistance of the DOE EPSCoR traineeship. Thanks go to the University of Kentucky Department of Geological Sciences and the University of Kentucky Center for Applied Energy Research for significant contributions of funds and access to equipment.

References

1. Derbyshire, F.J., Jagtoyen, M., McEnaney, B., Rimmer, S.M., Stencel, J.M., Thwaites, M.W., Proceedings 1991 ICCS Conference, 480-483, Newcastle, England, 16-20 September, 1991, Butterworth-Heinemann Ltd, 1991.
2. Derbyshire, F.J., Jagtoyen, M., McEnaney, B., Sethuraman, A.R., Stencel, J.M., Taulbee, D., and Thwaites, M.W., American Chemical Society, Fuel Division Preprints, **36** (3), 1072-1080, 1991.
3. Jagtoyen, M., McEnaney, B., Stencel, J.M., Thwaites, M.W., and Derbyshire, F.J., American Chemical Society, Fuel Division Preprints, **37** (2), 505-511, 1992.
4. Jagtoyen, M., Thwaites, M.W., Stencel, J.M., McEnaney, B., and Derbyshire, F.J., Carbon, **30** (7) 1089-1096, 1992.
5. Jagtoyen, M., Toles, C., Derbyshire, F.J., Fuel Division Preprints, American Chemical Society **38**, 400, 1993.
6. Jagtoyen, M., Derbyshire, F.J., Carbon, **31** (7) 1185-1192, 1993.

Table 1. Maceral composition of hand-picked Stockton bench 2.

Maceral	% Composition (mineral matter free)
Telocollinite	70.5
Desmocollinite	23.0
Pyrofusinite	2.5
Semifusinite	2.0
Exinite	2.0

Table 2. Composition and porosity of samples in this study.

HTT/Treatment	%Rmax	Atomic H/C	BET S.A. (m ² /g)
Parent	0.8	0.06	000
350°C/Acid	1.4	0.05	000
350°C/Thermal	1.0	0.06	000
450°C/Acid	2.0	0.04	110
450°C/Thermal	1.5	0.04	000
550°C/Acid	2.5	0.02	361
550°C/Thermal	2.8	0.03	000

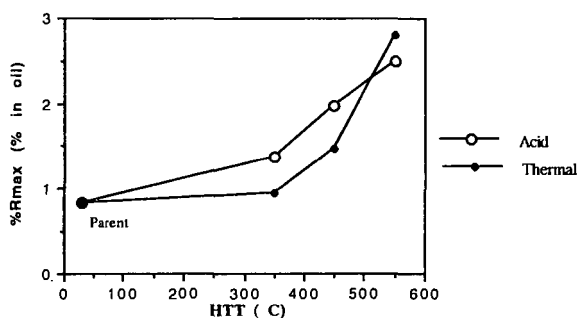


Figure 1: Relationship between reflectance and HTT for carbons produced from Stockton vitrinite-concentrate

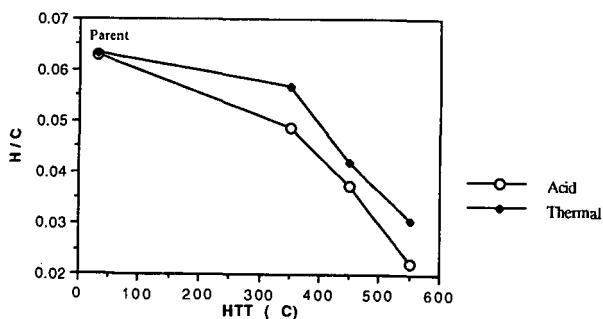


Figure 2: Relationship between H/C and HTT for Stockton vitrinite-concentrate

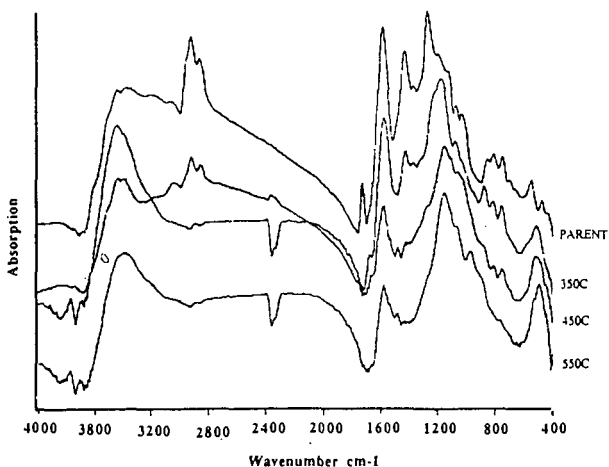


Figure 3: FTIR spectra for acid treated carbons (top) and thermal counterparts (bottom) from vitrain concentrates.

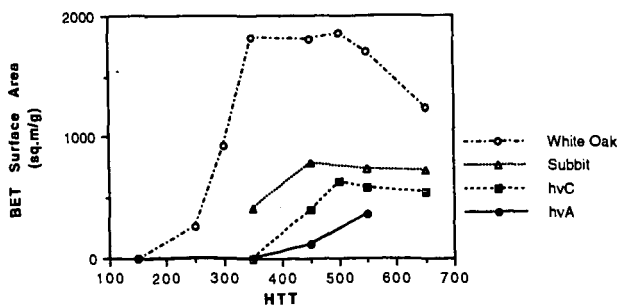


Figure 4: Surface area related to parent material [modified after ref. 6]

ADDING VALUE TO COAL CONVERSION'S CHAR:
A STRATEGY FOR LOWER-PRICED FUELS

Carl W. Kruse
Illinois State Geological Survey
615 E. Peabody, Champaign, IL 61820

Mohammad Fatemi
Amoco Corporation
Amoco Research Center, P.O. Box 3011
Naperville, IL 60566

Cuneyt Feizoulouf
Civil Engineering Department
University of Illinois
Urbana, Illinois 61801

Keywords: Char, activated carbon, adsorbent, catalyst

INTRODUCTION

Coal's low hydrogen to carbon ratio gives coal physical properties that are not the most desired in fuel markets. The problem is dealt with in conversion technologies designed to upgrade coal to more desirable fuels by either: 1) chemically adding hydrogen, as in liquefaction or high-BTU gasification, or 2) the production of char, as in mild gasification. The first option is neither cost-effective nor environmentally sound. Liquefaction results in the production of one mole of carbon dioxide for each mole of hydrogen needed. The result is that despite the preferred hydrogen to carbon ratio in the fuel, carbon dioxide is produced in greater quantities than it would be by simply burning the coal. The depressed market value of char is the primary drawback of coal utilization technologies exercising the second option. Making value-added, non-fuel products from char could significantly improve the economics of overall operations and result in competitively-priced premium hydrocarbon fuels. The research goal of a growing number of groups, including ours, is to produce and describe carbon products which will command higher prices than the carbon (coal) from which they were produced.

Opportunities for developing specialty chemicals and advanced materials from coals were recently reviewed (Song and Schobert, 1993). One- to four-ring aromatics from coal may be necessary to feed the rapidly growing engineering applications of aromatic polymer materials. Development of high-performance carbon materials, such as carbon fibers, graphites, and advanced adsorbents for environmental applications, is another approach for moving coal's carbon into non-fuel uses (Economy et al., 1992; Thwaites et al., 1993). Carbons suitable for methane storage are being produced (Quinn and MacDonald, 1992). Carbon molecular sieves manufactured for commercial pressure swing adsorption (PSA) systems are now competing with zeolites for air separation applications. Illinois Basin coals have been shown to be good feedstocks for making molecular sieves from coal (Lizzio and Rostam-Abadi, 1993). Europeans and Japanese are reportedly testing carbons for adsorption of radon (Kinner et al., 1993; Nakayama et al., 1993). There are biotechnology applications involving carbon as a support material (Rittmann, 1993). Commercial use of activated carbon to reduce SO_2 , NO_x , and mercury in the flue gas from waste incineration plants is well-advanced in Germany (Brueggendick and Pohl, 1993) and Japan (Tsuji and Shiraishi, 1991). Oxidized activated char catalysts have not only the capacity to adsorb volatile organic chlorides but, when heated, they catalyze decomposition of the adsorbed chlorides (Fatemi et al., 1993).

This paper describes a portion of ongoing efforts to differentiate between types of oxidized carbon surfaces, especially those that have catalytic activity for elimination reactions, and those that have selective adsorptive properties for organics in the aqueous phase. It is motivated by the belief that identifying now the uses for high-quality carbon will stimulate future demands. Demands for non-fuel uses of coal will pull coal toward the market place rather than having to push products on reluctant buyers who may presently consider coal products inferior.

Oxidized carbon surfaces were discovered in the 1960s to be catalysts for elimination of hydrogen chloride from alkyl halides and alkylation of aromatics (Kruse and Ray, 1966; Mahan et al., 1967; Kruse, 1969). Brief exposure to air at 550-700°C was shown to activate a wide variety of carbon substrates. Heating to 950°C destroyed all catalytic activity. Amines and potassium salts modified the selectivity of these catalysts. Other workers reported later that inactive carbon surfaces could be made active for catalysis of oxidation reactions and hydrogen halide elimination

reactions by treatment with ammonia or HCN at elevated temperatures (Boehm et al., 1984). Substitution of carbon by nitrogen atoms at the edges of the carbon sheets was postulated to be responsible for the catalytic properties. Recent studies have revealed that nitrogen incorporated in activated carbons increases resistance to burn-off with CO₂ at 850°C (Mang et al., 1992). The rate of gasification did not correlate directly with the nitrogen content. Gasification rates with 5% O₂ in argon of four carbons at temperatures between 500°C and 650°C showed the rate was significantly reduced by nitrogen at 500°C. Curves describing burn-off rates became steeper for the nitrogen-enriched chars at higher temperatures. Above 570°C a carbon prepared from a mixture of sugar and glucosamine was oxidized more rapidly than the reference sample. Enrichment of nitrogen in the remaining carbon during the combustion of carbons has been seen previously (Spracklin et al., 1991).

We report our observations of differences in surface nitrogen, oxygen and sulfur for a series of carbons as determined by X-ray Photoelectron Spectroscopy (XPS). XPS has been widely applied to study the surfaces of organic materials. Surface chemistry, which is frequently determined by varying the types of functional groups, may be revealed by XPS. Different functionalities containing oxygen, nitrogen, and sulfur can be quantitatively identified by XPS. Moreover, changes in surface functionalities due to chemical modifications can also be studied.

EXPERIMENTAL

Seven samples were prepared from granular activated carbon (GAC), Filtrasorb-400 (F-400), designated herein as AR000, manufactured from a bituminous coal by the Calgon Corporation. Proximate and ultimate analyses were made with a LECO Mac-400 and a LECO CHN-600, respectively. Brunauer, Emmett, and Teller (BET) surface area, micropore volume and mesopore volume were all calculated for nitrogen adsorption isotherms obtained at 77K using a Micromeritics Nitrogen Surface Analyzer 2400 ASAP. See Table 1.

AR000 was placed in an acid washing column and washed with 10 bed volumes of 1.0 M hydrochloric acid followed by 10 bed volumes of 1.0 M nitric acid. The carbon was then rinsed with 20 bed volumes of deionized water followed by 5 bed volumes of a carbonate solution buffered at pH 6. The carbon was then rinsed with 5 bed volumes of distilled-deionized water. The acid-washed AR000 was fluidized in ultra-high-purity (UHP) N₂ at 950°C for 30 minutes to produce the sample designated FN950, from which six samples were prepared by the methods given in Table 2. Two additional samples, SA10-14 and OSA10-14, described previously (Kruse et al., 1992), were made from a mixture of Illinois No. 5 and No. 6 coals. The oxidized steam-activated char (OSA10-14) was active as a dehydrochlorination catalyst.

Table 1. Characterization of AR000

<u>Proximate analysis</u> ¹	
Moisture	1.1
Volatile Matter	5.4
Fixed Carbon	88.3
H-T Ash	6.2
<u>Ultimate analysis</u> ¹	
Hydrogen	0.25
Carbon	91.80
Nitrogen	0.72
Oxygen	0.40
Sulfur	0.59
BET Surface Area ²	1035 m ² /g
Micropore Volume ²	0.421 cc/g
Mesopore Volume ²	0.231 cc/g

¹ moisture-free basis

² moisture ash-free basis

XPS involves irradiation of a sample with monoenergetic x-rays resulting in subsequent emission of photoelectrons. By determining the kinetic energies of the emitted electrons, the characteristic binding energies that are dependent on the local chemical environment can be calculated. Since the escape depth is 30-60 Å, XPS is a surface sensitive technique. Functional groups and the binding energies (eV) associated with them are: elemental and organic sulfur species at 164.2±0.2, sulfates and sulfonates at 168.3±0.3, amines and pyridines at 398±0.3, pyrolic nitrogen, amides and amino groups at 400.2±0.3, ammonium derivatives at 401.2±0.3, nitrates at 405.9±0.7, metal oxides at 529.5±0.2 and 531.5±0.2, numerous special carbon-oxygen species and superoxide (O₂⁻ ions) at 533.2±0.2. Surface compositions (% atomic) calculated from XPS analyses for atoms appearing in amounts greater than 0.1% are given in Table 2 and the binding energies of selected atoms in this same group in Table 3.

DISCUSSION OF RESULTS

The adsorption characteristics of the carbons described herein were reported earlier this year (Feizoulouf et al., 1993). It was found that the adsorptive capacity for p-nitrophenol increased as oxygen-containing functional groups put onto the carbon by nitric acid oxidation were removed by temperature programmed desorption.

The variation in carbon's fraction of atoms on the surfaces of the samples (see Table 2) is related to coverage by oxygen for the first eight samples and to ash-forming constituents in the last two.

Among the distribution of C 1s binding energies, it appears that the sample OSA10-14, the catalyst, has the highest fraction of carbon-oxygen functional (C-O and C=O) groups. The oxygen pattern is that to be expected, except for DS950. Fluidization at 950°C with nitrogen (FN950) produced the lowest surface oxygen, stripping away some of the oxygen on the as-received carbon. Brief air oxidation at 300°C introduced some oxygen (AO305) and boiling nitric acid even more (HN100). Some of this oxygen on HN100 was in the form of nitrates. This sample's nitrogen value was higher than any other and it had a 405.9 eV XPS peak indicative of nitrates. This extra nitrogen was lost in desorption at 405 °C (DS405). Oxygen drops to the lowest values as the desorption is continued through two higher temperatures where carbon dioxide is known to be the primary gas evolved. The increase in oxygen for DS950 is believed to have occurred after the sample was cooled. The 168 eV sulfur binding peak, not seen in the DS525 or DS725, is associated with sulfates. This is additional evidence that DS950 underwent oxidation after preparation at 950°C and prior to XPS analyses. No conclusions are drawn from the distribution of O 1s binding energies; the lack of resolution of types for the last two samples, run at a different time by a different operator, are not considered significant.

The coverage by nitrogen is approximately constant ($0.67 \pm 0.15\%$), within the accuracy of the determination at this low percentage, for nine samples (excluding HN100). Binding energies for N 1s are similar, except for HN100, which has a nitrate peak, and FN950, which shows some differentiation in the 398-400 eV range not observed elsewhere. The ratio of types of nitrogen functionalities remaining after nitrates have been removed by heating to 405°C is not what one would project by simple subtraction. There may be a transformation of material initially responsible for a part of the 400.5 eV peak to new material having a 401 eV binding energy. Decomposition of amides is a possibility. Sulfur coverage is constant for the first eight samples and much higher for the two chars from high sulfur coal, as expected. The absence of sulfate in the last two samples is surprising considering how easily sulfate appears to form in the first eight, but this too may be a difference in instrument calibration by different operators.

XPS binding energies at *ca.* 400 eV, usually associated with amino groups or amides, and at *ca.* 398 eV, typically associated with nitrogen bound in aromatic rings in pyridine-like fashion, were reported for three carbons having differing nitrogen contents. The peak at 398 eV was much higher with NH_3 -treated carbons but neither signal was reported to be associated with catalytic activity of the carbons (Mang et al., 1992; Stohr et al., 1991). We too find no correlation between the dehydrochlorination activity of an oxidized-carbon catalyst, OSA10-14, and the surface functional groups as determined by XPS.

If nitrogen atoms contribute to the catalytic properties of oxidized carbons discovered in the 1960s, those nitrogen atoms are likely those already present in the materials. We are unaware of evidence that indicates the fixation of nitrogen in burning carbonaceous material in air at 500-700°C. If the nitrogen inhibition reported by Mang and others is spatially limited to areas adjacent to bound nitrogen atoms, the nitrogen-containing formations could be left in relief on surface areas. This effect would be most pronounced at temperatures for which the rates of gasification differ the most for nitrogen-containing structures compared to nitrogen-free zones. Depending on the dimensions of the volume affected by the nitrogen, the distribution of nitrogen atoms, and the degree of gasification, nitrogen-containing functional groups would be generated on pore wall surfaces.

It is postulated that the observed catalytic activity may be the result of specialized spatial arrangements of specific functional groups within the pores of the carbon. XPS would not reveal special spatial arrangements of two or more functional groups on pore walls which may be responsible for catalysis. Figure 1 diagrams one of many arrangements that could catalyze elimination in high yields without rearrangement of the carbon skeleton. This lack of rearrangement was of special importance to the industrial research goals in the 1960s because biodegradability of commercial detergents depended on preserving the linearity of the olefins.

CONCLUSIONS

Failure to correlate surface functional groups, identified by XPS, with catalyst activity is not unexpected if activity is dependent on functional groups located on critically-spaced opposing surfaces of pores. If catalyst sites are internal,

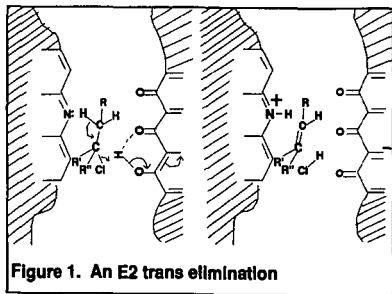


Figure 1. An E2 trans elimination

determining adsorption differences and increased strengths of adsorption due to chelation between properly spaced groups may be more fruitful. The use of Mossbauer Spectroscopy to follow field effects of the type studied with tin is another possibility (Larsen et al., 1982). Future work should include monitoring the evolution of nitrogen oxides in TPD analyses in addition to CO₂ and CO to determine what combination of groups may be involved.

ACKNOWLEDGMENTS

This was supported in part by grants made possible by the Illinois Department of Energy and Natural Resources (ENR) through its Coal Development Board and the Illinois Clean Coal Institute (ICCI), and from the United States Department of Energy (Grant Number R 91-1/1.1B-4M). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of ENR, ICCI, and the DOE. The ICCI project managers were Frank Honea and Daniel Banerjee. In-kind contributions by the Alternative Feedstock Development (AFD) program of Amoco Corporation are gratefully acknowledged. Without this support and the encouragement of R. E. Lumkin (AFD), this work would not have been possible. The authors acknowledge contributions by ISGS staff members Massoud Rostam-Abadi, Anthony Lizzio, Ilham Demir and Steve Carlson.

REFERENCES

- Boehm, H. P., G. Mair, T. Stoehr, A.R. De Rincon, B. Tereczki 1984 Carbon as a catalyst in oxidation reactions and hydrogen halide elimination reactions *Fuel* **63** (8) 1061-3.
- Brueggendick, H., F.G. Pohl 1993 Operating experience with Steag's activated carbon processes-a/chTM. in European waste incineration plants *Brochure published by Steag AG, Huyssenalle 88, D-45128 Essen, Germany.*
- Economy, J., K. Foster, A. Andreopoulos, H. Jung 1992 Tailoring carbon fibers for adsorbing volatiles *Chemtech* **October** 597-603.
- Fatemi, S.M., C.W. Kruse, R.T. Lagman 1993 Oxidized activated char as an adsorbent and catalyst *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo* June 13-18 505-506.
- Feizoulouf, C., V.L. Snoeyink, C.W. Kruse 1993 The effect of carbon surface chemistry on enhanced adsorption of a targeted compound from water *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo, June 13-18* 367-368.
- Kinner, N.E., J.P. Malley, J.A. Cement, K.R. Fox 1993 Using POE techniques to remove radon *Journal-American-Water-Works-Association* **85** (6) 75-86.
- Kruse, C.W., G.C. Ray 1966 Dehydrohalogenation of hydrocarbon halides *US Patent* 3,240,834 Mar. 15.
- Kruse, C.W. 1969 Polymerization *US Patent* 3,437,695 April 8.
- Kruse, C.W., M.I.M. Chou, C. Feizoulouf, M. Fatemi, P. Beaulieu 1992 Oxidized coal char as a catalyst: characterization *Preprints of Papers Presented at San Francisco, CA ACS Div. of Fuel Chemistry, April 5-10* **37** (2) 556-563.
- Larsen, J.W., P.A. Nadar, M. Mohammidi, P.A. Montano, P.A. 1989 Spatial distribution of oxygen in coals. Development of a tin labelling reaction and Mossbauer studies *Fuel* **61** (10) 889-893.
- Lizzio, A.A., M. Rostam-Abadi 1993 Production of carbon molecular sieves from Illinois coal *Fuel Processing Technology* **34** 97-122.
- Mahan J.E., R.E. Reusser, C.W. Kruse 1967 Dehydrohalogenation process *US* 3,352,935, November 14.
- Mang, D., H.P. Boehm, K. Stanczyk and H. Marsh 1992 Inhibiting effect of incorporated nitrogen on the oxidation of microcrystalline carbons *Carbon* **30** (3) 391-398.
- Nakayama, Y., H. Nagao, M. Mimura, H. Yamasita, E. Tanaka, K. Hosokawa 1993 Radon adsorption in activated carbon related to specific surface area and water absorbing *Abstracts of papers at 21st Biennial Conference on Carbon, State University of New York at Buffalo, June 13-18* 402-403.
- Quinn, D.F., J.A. MacDonald 1992 Natural gas storage *Carbon* **30** 1097-1103.
- Rittmann, B.E. 1993 The significance of biofilms in porous media *Water Resources Research* **29** 2195-2202.
- Song, C., H.H. Schobert 1993 Opportunities for developing specialty chemicals and advanced materials from coals *Fuel Processing Technology* **34** 157-196.
- Spracklin, C.J., K.M. Thomas, H. Marsh, I.A.S. Edwards 1991 Nitrogen functionality in carbons and its release as NO_x during gasification *Abstracts of papers at 20th Biennial Conference on Carbon, Santa Barbara, California* 212-213.
- Stohr, B., H.P. Boehm, R. Schlögl 1991 Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate *Carbon* **29** 707.
- Thwaites, M.W., M.L. Stewart, B.E. McNeese, M.B. Summer 1993 Synthesis and characterization of activated pitch-based carbon fibers *Fuel Processing Technology* **34** 137-145.
- Tsuji, K., I. Shiraishi 1991 Mitsui-BF dry desulfurization and denitrication process using activated coke in *Proceedings of the EPRI SO₂ Control Symposium, Washington D.C.* 307-324.

Table 2 Surface composition (% atomic) by XPS

ID #	Description	C	O	N	S	Si
AR000	Calgon F400 commercial activated carbon	88.8	9.7	0.6	0.2	0.5
FN950	Acid-washed AR000 fluidized in high purity N ₂ at 1223 K for 30 min.	90.8	7.2	0.8	0.2	0.4
AO305	FN950 oxidized, 573 K, 10% O ₂ /90% N ₂ , 5 min	90.5	8.1	0.7	0.2	0.4
HN100	FN950 oxidized with 1.0 M HNO ₃	87.7	10.1	1.1	0.2	0.5
DS405	HN100 outgassed at 678 K in high purity N ₂	88.1	10.3	0.7	0.2	0.4
DS525	HN100 outgassed at 798 K in high purity N ₂	91.1	7.4	0.5	0.2	0.5
DS725	HN100 outgassed at 998 K in high purity N ₂	90.6	7.7	0.7	0.2	0.5
DS950	HN100 outgassed at 1223 K in high purity N ₂	87.8	10.4	0.7	0.3	0.5
SA10-14 ¹	Steam-activated, Illinois coal char ² , 1123 F 50% steam/50% nitrogen	80.0	10.4	0.5	3.7	2.6
OSA10-14 ¹	SA10-14 Oxidized at 723 K, 10% O ₂ /90% N ₂ , 15 min	80.0	10.2	0.8	3.9	2.3

¹ Al 1.6%, Fe 0.8%, Ca 0.3%.² A mixture of Illinois No 6 and No 5 coals charred at 500 °C

Table 3. Binding Energies (eV) from XPS Analyses of the Original and Treated Calgon F-400 Activated Carbon Samples

Sample ID	C 1s %	O 1s %	N 1s %	S 2p %
AR000	284.6 62	531.5 52	399.4 27	164.4 71
	286.0 21	533.3 48	401.4 73	168.6 29
	288.9 17			
FN950	284.6 62	531.5 32	397.9 11	164.2 61
	286.0 22	533.2 68	399.8 51	168.6 39
	288.9 16		401.3 38	
AO305	284.6 66	531.5 32	399.3 35	164.2 77
	286.1 19	533.2 68	401.2 65	168.6 23
	289.2 15			
HN100	284.6 68	531.5 53	400.5 85	164.2 63
	286.2 18	533.2 47	405.9 15	168.4 37
	289.1 14			
DS405	284.6 58	531.6 32	399.3 31	164.1 84
	286.0 25	533.1 68	400.9 69	168.2 16
	288.7 17			
DS525	284.6 66	529.5 22	398.8 35	164.1 100
	286.1 22	531.5 35	401.1 65	
	289.6 12	533.2 43		
DS725	284.6 63	531.4 54	398.8 33	164.2 100
	286.0 21	533.3 46	401.2 67	
	289.2 16			
DS950	284.6 65	531.5 55	400.8 31	164.3 83
	286.0 21	533.3 45	401.2 69	168.3 17
	289.3 14			
SA10-14	284.6 64	533.2 100	398.6 22	163.9 100
	286.3 23		401.2 78	
	289.7 12			
OSA10-14	284.6 60	533.2 100	398.7 22	163.9 100
	286.0 30		402.3 78	
	290.0 10			

COAL/OIL COPROCESSING USING SYNGAS: EFFECTS OF D₂O DURING HYDRODESULFURIZATION

Yuan C. Fu, Katsuya Ishikuro, Makoto Akiyoshi
Department of Applied Chemistry
Muroran Institute of Technology
Muroran 050, Japan

Mitsuyoshi Yamamoto, Takeshi Kotanigawa
Government Industrial Development Laboratory, Hokkaido
Sapporo 061, Japan

Keywords: Hydrodesulfurization, Syngas, Deuterium Oxide

INTRODUCTION

It has been shown that coal liquefaction¹ and coprocessing^{2,3} of coal with petroleum solvents could be carried out using syngas (H₂+CO) and steam instead of hydrogen. High coal conversion could be obtained with considerable saving in hydrogen consumption. Earlier studies have also shown that model compounds could be hydrogenated and desulfurized in the presence of petroleum solvents and catalyst using syngas with steam. It was considered that the CO in the syngas reacts with steam to form hydrogen via water-gas shift reaction, and that the hydrogen formed could also participate in the hydrogenation of coal, but the fate of hydrogen formed from the water-gas shift reaction was not known. It is known that deuterium is incorporated into reaction products during coal liquefaction under D₂ gas⁴, and that hydrogen/deuterium transfer occurs among solvent, reaction products and gas when deuterium-labeled solvents are used in coal liquefaction experiments⁵.

This study deals with hydrodesulfurization of a sulfur-containing model compound using syngas and steam. In order to understand the roles of molecular hydrogen and water in the syngas system during the hydrodesulfurization, experiments were carried out to treat dibenzothiophene in the presence of solvent and catalyst under pressure using H₂-CO-D₂O, D₂-CO-H₂O and N₂-D₂O systems. Deuterium gas and D₂O were used in an effort to study the incorporation of hydrogen from the gas and water by tracing the migration of deuterium through the system.

EXPERIMENTAL

The hydrodesulfurization of dibenzothiophene was conducted in a shaking 25-ml microreactor in the presence of decalin solvent and a commercial NiMo/Al₂O₃ catalyst (Nippon Mining Co.) using syngas and water at an initial pressure of about 70 kg/cm² in most cases. The reactor was quickly heated up in a fluidizing sand bath and maintained at 400°C for 45 minutes, and then rapidly quenched in a cold water bath. Various H₂:CO:H₂O mole ratios with H₂/CO mole ratios varying from 1 to 3 and H₂O/CO mole ratios varying from 0.3 to 1.0 were used. For the experiments, a mixture of 30 parts of dibenzothiophene and 70 parts of solvent was placed in the microreactor, 10 weight % (based on the mixture) of ground presulfided catalyst was charged, and calculated amount of water was added before the reactor was pressured with syngas. After the reaction, the liquid products were analyzed by a Shimadzu GC-14A gas chromatograph using OV-1 fused silica capillary column (60m×0.25mmφ), and gaseous products were analyzed by a Shimadzu GC-14A gas chromatograph.

In experiments using D₂ gas and D₂O, an initial pressure of about 40 kg/cm² was used because of low pressure available for the D₂ bomb. The liquid products were analyzed by a Shimadzu QP-1000 gas chromatograph-mass spectrometer. Spectral analysis was performed using the known split patterns of various undeuterated compounds. For these runs, samples of the gaseous products were obtained by passing through a dry ice and acetone trap to remove moisture prior to analysis using gas chromatograph and a ULVAC MSQ-150A quadrupole mass analyzer. For hydrogen analysis, relative intensities of peaks of molecular ions were used to estimate the relative portions of H₂, HD, and D₂.

RESULTS AND DISCUSSION

Hydrodesulfurization of Dibenzothiophene in Various Solvents. During coal liquefaction, large coal molecules fragment thermally and are hydrogenated via hydrogen transfer from a donor solvent. Coprocessing of coal with petroleum solvents using either hydrogen or syngas with steam was also aided by the presence of tetralin³. Dibenzothiophene was initially hydrodesulfurized in the presence of various solvents including decalin, tetralin, and a mixture of decalin and an aromatic compound. The results of hydrodesulfurization carried out under hydrogen and syngas pressures are shown in Table 1. Dibenzothiophene was easily hydrogenated and desulfurized by hydrogen to form mainly biphenyl, cyclohexylbenzene, bicyclohexyl, and decomposed products. Tetralin donated some hydrogen to form naphthalene, but was also hydrogenated to form decalin. Decalin converted to small amounts of tetralin and naphthalene. An aromatic compound was added with an intention of finding out the effects of aromatic compounds on hydrogen transfer between decalin and dibenzothiophene. The hydrogenated products from 1-methylnaphthalene was not included in the table. When an aromatic compound was added to decalin as the solvent, the effect on the product distribution was not conclusive, but high dibenzothiophene conversions were obtained with all solvents. It appears that catalytic hydrogenation by hydrogen gas plays the dominant role with respect to the hydrodesulfurization.

When dibenzothiophene was treated with syngas and steam ($H_2:CO:H_2O=1:1:0.3$), the hydrogenation and desulfurization activities were lower. The yields of hydrogenated products, cyclohexylbenzene and bicyclohexyl, were lower. These results indicate that the performance of syngas in hydrodesulfurization did not come up to the satisfactory level that was observed in coal liquefaction. In coal liquefaction, the performances with syngas and H_2 compare rather closely except that asphaltene levels of the syngas products were somewhat higher¹.

Table 2 shows the results of hydrodesulfurizing dibenzothiophene using decalin solvent and syngas with steam at various $H_2:CO:H_2O$ ratios. The dibenzothiophene conversion increased with H_2/CO mole ratio, while H_2O/CO mole ratio was maintained at 0.6. The data indicate that the H_2O level at the H_2O/CO mole ratio of about 0.6 is appropriate or about optimum to give better results yielding more hydrogenated products. The extent of water-gas shift reaction was rather extensive as can be seen from high CO conversions obtained in all runs. The CO conversions were calculated on the basis of the amounts of CO_2 formed. As was observed in coal liquefaction and coprocessing using syngas, H_2 formation via water-gas shift reaction resulted in reduction of hydrogen consumption and increase of H_2/CO mole ratio after the reaction.

Hydrodesulfurization Using Syngas Containing D_2O and D_2 . Experiments with syngas containing D_2O and D_2 were carried out to observe how the hydrogen transfer reactions occurred from H_2O and gas-phase hydrogen. Dibenzothiophene was hydrodesulfurized in the presence of decalin solvent using $H_2-CO-D_2O(1:1:1)$ and $D_2-CO-H_2O(1:1:1)$ gas systems as shown in Table 3. Another experiment using $N_2-D_2O(2:1)$ system was also carried out. Initial pressures of syngas and N_2 used were lower (about 40 kg/cm²) in this series of experiments because only a limited pressure of D_2 gas was available. Similar to the results shown in Table 2, both the hydrodesulfurization and water-gas shift reaction progressed moderately. In the experiment using N_2-D_2O system, some dibenzothiophene decomposed to form biphenyl, and the formation of naphthalene from decalin increased.

The reaction products and remaining solvents were analyzed using GC-MS, and deuterium distributions in the products and solvents are shown in Figure 1. In the H_2-CO-D_2O system, the cyclohexylbenzene product was deuterated extensively to form d_2 , d_3 , d_4 , d_5 , and d_6 species, but no d_0 or d_1 species was present. Deuterium was also distributed widely to the biphenyl product, and all species from d_0 to d_6 were present. Large parts of cis-decalin was isomerized to trans-form, but both forms similarly contained about 30% of d_1 -decalin. Only trans-decalin was shown in Figure 1. The H/D exchange of D_2O with the decalin solvent

was not as extensive as that with the products. In the D_2 -CO- H_2O system, it was noted that deuterium was incorporated only moderately into cyclohexylbenzene and biphenyl, both forming d_1 , d_2 , and d_3 species. Only about 20% of d_1 species was present in either trans- or cis-decalin. It is of interest to observe that, under N_2 pressure, H/D exchange occurred extensively between D_2O and dibenzothiophene. Even though the amounts of cyclohexyl and biphenyl formed were smaller, deuterium was incorporated into these products more extensively than was observed in the D_2 -CO- H_2O system. Although not shown in the figure, the spectra of the unreacted dibenzothiophene obtained from the experiments carried out in the H_2 -CO- D_2O and N_2 - D_2O systems indicated that they were all D-substituted species containing d_1 , d_2 , d_3 , and d_4 species. However, it was observed that the unreacted dibenzothiophene obtained in the D_2 -CO- H_2O system was nothing but the d_1 species.

The extensive H/D exchange observed between dibenzothiophene and D_2O under N_2 pressure is consistent with the results reported by Kabe et al⁶ dealing with hydrogen exchange of H_2O with coal or phenolic model compounds. In the case dealing with hydrogen exchange between syngas- H_2O and dibenzothiophene, the situation is not the same. Water participates in the water-gas shift reaction as evidenced by the formation of CO_2 . It is expected that the D_2O in the syngas- D_2O system reacts with CO to form active deuterium which leads to the formation of D_2 , and in the process, some active deuterium may be incorporated into dibenzothiophene and the substrates.

To observe the extent of D atoms from D_2O transfer back to form dihydrogen such as HD and D_2 in gaseous products, the gases were analyzed by gas chromatograph and quadrupole mass spectrometer. The analytical results are given in Table 4. It is noted that some deuterium in D_2O is present in HD and D_2 in the syngas- D_2O system, while no deuterium is present in the "hydrogen gases" of the gaseous products in the N_2 - D_2O system. A small amount of H_2 formed in the N_2 - D_2O system may have come from the dehydrogenation or decomposition of the solvent and reactant. In contrast to the experiment in the H_2 -CO- D_2O system where HD and D_2 were formed, the experiment in the D_2 -CO- H_2O system yielded gaseous products containing HD and H_2 in the "hydrogen gases". These results indicate that, unlike D_2O in the N_2 - D_2O system, D_2O in the syngas- D_2O system or H_2O in the D_2 -CO- H_2O system forms active deuterium or hydrogen, respectively, which in turn is incorporated into the reactant and substrates or leads to the formation of HD and D_2 or HD and H_2 , respectively. In the N_2 - D_2O system, most deuterium is probably incorporated into the reactant by exchange reactions. It may then be concluded that both gas-phase hydrogen and hydrogen formed via the water-gas shift reaction in the syngas- H_2O system contribute to hydrodesulfurization, and the accompanying water-gas shift reaction is beneficial in reducing H_2 consumption.

ACKNOWLEDGEMENTS

We thank the support of Grant-in Aid of Scientific Research provided by the Ministry of Education, Japan.

REFERENCES

1. Batchelder, R.F., Fu, Y.C., Ind.Eng.Chem. Process Des. Dev. Vol.18, No.4, 594(1979)
2. Fu, Y.C., Akiyoshi, M., Tanaka, F., Fujiya, K., Preprints, Div. Fuel Chem., Am.Chem.Soc. Vol.36, No.4, 1887(1991)
3. Fu, Y.C., Tanabe, K., Akiyoshi, M., Preprints, Div. Fuel Chem., Am.Chem.Soc. Vol 37, No 4, 1776(1992)
4. Skowronski, R.P., Ratto, J.J., Goldberg, I.B., Heredy, L.A., Fuel, Vol 63, 440(1984)
5. Cronauer, D.C., McNeil, R.I., Young, D.C., Ruberto, R.G., Fuel, Vol 61, 610(1982)
6. Ishihara, A., Takaoka, H., Nakajima, E., Imai, Y., Kabe, T., Energy & Fuels, Vol 7, 362(1993)

Table 1. Hydrodesulfurization of Dibenzothiophene
(Catalyst: NiMo/Al₂O₃, Initial Press: 70 kg/cm², Temp: 400 °C, Time: 45 min)

Gas system Solvent	H ₂			H ₂ -CO-H ₂ O (1:1:0.3)		
	Decalin	Tetralin	Decalin + 1-methyl- naphthalene	Decalin	Tetralin	Decalin + 1-methyl- naphthalene
Dibenzothiophene conv., %	94.2	94.1	94.8	74.8	77.1	80.4
Bicyclohexyl formed, %	7.4	3.8	3.8	0.3	1.2	1.0
Cyclohexylbenzene formed, %	24.8	32.6	30.8	21.2	21.1	16.6
Biphenyl formed, %	33.6	39.5	43.8	42.0	44.0	54.5
Decalin remained, %	84.2	16.9 ^a	83.8	91.2	4.3 ^a	89.4
trans/cis ratio	4.8	4.0	4.5	4.0	3.7	4.1
Tetralin formed, %	2.9	67.2 ^b	5.0	3.8	75.3 ^b	4.8
Naphthalene formed, %	0.2	7.0	1.6	1.1	18.4	2.0
1-Methylnaphthalene remained, %	-	-	22.9	-	-	51.5
CO conv., %	-	-	-	32.5	40.3	39.8
H ₂ consump., wt% of dibenzothiophene	5.2	6.0	7.3	2.0	2.0	3.4

^aDecalin formed

^bTetralin remained

Table 2. Hydrodesulfurization Using Syngas at Various H₂/CO/H₂O Mole Ratios
(Catalyst: NiMo/Al₂O₃, Solvent: Decalin, Temp: 400 °C, Time: 45 min)

Syngas-H ₂ O	H ₂ -CO-H ₂ O (1:1:0.3)	H ₂ -CO-H ₂ O (1:1:0.6)	H ₂ -CO-H ₂ O (1:1:1)	H ₂ -CO-H ₂ O (2:1:0.6)	H ₂ -CO-H ₂ O (3:1:0.6)
Initial syngas press., kg/cm ²	70	63	55	70	70
Dibenzothiophene conv., %	74.8	72.0	63.7	78.7	81.0
Bicyclohexyl formed, %	0.3	1.5	0.6	2.5	2.8
Cyclohexylbenzene formed, %	21.2	20.6	14.6	24.1	26.1
Biphenyl formed, %	42.0	41.5	44.5	36.7	36.8
Decalin remained, %	91.2	92.2	92.2	91.4	92.8
trans/cis ratio	4.0	4.0	3.8	4.3	4.3
Tetralin formed, %	3.8	4.1	4.6	3.0	3.2
Naphthalene formed, %	1.1	1.1	1.9	0.4	0.5
CO conv., %	32.5	34.7	26.6	25.8	35.3
H ₂ consump., wt% of dibenzothiophene	2.0	0.9	0.1	1.6	2.7
H ₂ /CO ratio after the reaction	1.5	1.6	1.4	2.7	5.2

Table 3. Hydrodesulfurization Using Syngas-D₂O or Deuterium Containing Gases
(Catalyst: NiMo/Al₂O₃, Solvent: Decalin, Temp: 400 °C, Time: 45 min)

Gas system	H ₂ -CO-D ₂ O (1:1:1)	D ₂ -CO-H ₂ O (1:1:1)	N ₂ -D ₂ O (2:1)
Initial press., kg/cm ²	40	40	40
Dibenzothiophene conv., %	74.5	69.5	35.0
Bicyclohexyl formed, %	0.6	0.3	trace
Cyclohexylbenzene formed, %	14.1	11.4	0.2
Biphenyl formed, %	43.9	45.4	27.2
Decalin remained, %	84.0	87.0	82.6
trans/cis ratio	3.8	4.0	2.2
Tetralin formed, %	5.5	5.3	3.7
Naphthalene formed, %	2.5	2.9	7.1
CO conv., %	30.1	23.3	-

Table 4. G. C. and M. S. Analysis of Gaseous Products

Gas system	H ₂ -CO-D ₂ O	D ₂ -CO-H ₂ O	N ₂ -D ₂ O
Gaseous Products*, mol %			
CO	40.1	35.2	-
CO ₂	15.0	12.7	-
N ₂	-	-	94.0
Hydrogen	41.3	48.7	3.6
(H ₂)	(63)	(13)	(100)
(HD)	(31)	(11)	0
(D ₂)	(6)	(76)	0

* The remainders are CH₄, C₂H₆, and H₂S.

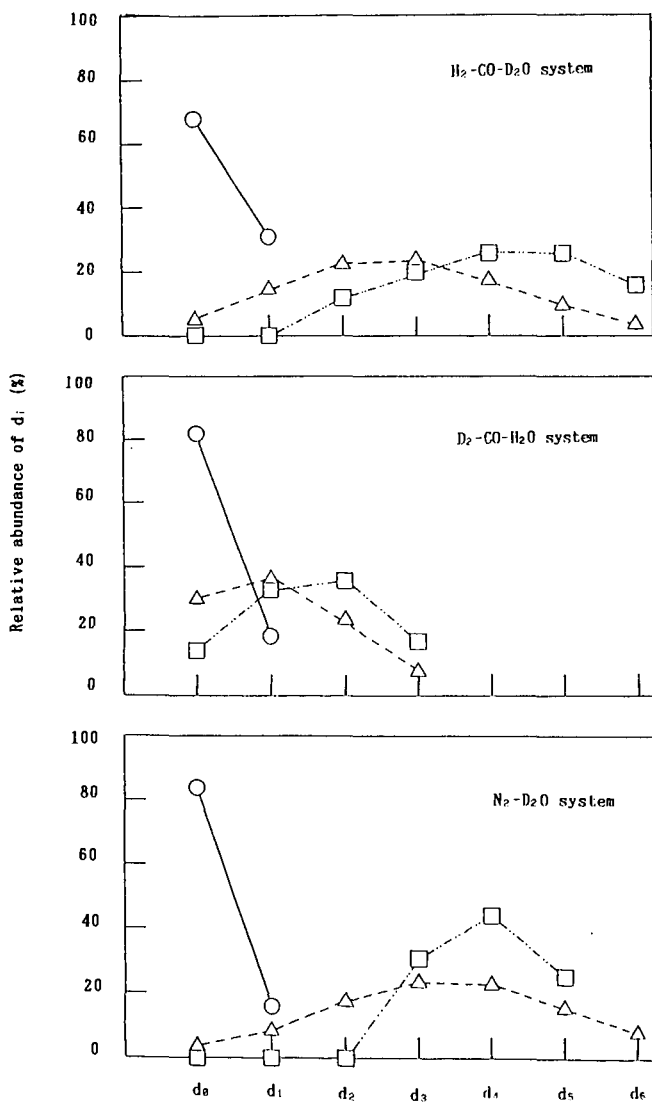


Figure 1 Distribution of deuterium in solvent and products
 ○ t-Decalin △ Biphenyl □ Cyclohexylbenzene

HDS ACTIVITY AND SURFACE PROPERTY OF ALUMINA-SUPPORTED RUTHENIUM CATALYST

Masatoshi Nagai and Kenji Koizumi
Department of Chemical Engineering,
Tokyo University of Agriculture and Technology,
Koganei, Tokyo 184, Japan

Keywords: HDS, $\text{Ru}/\text{Al}_2\text{O}_3$, NH_3 -TPD

INTRODUCTION

Ruthenium and its compounds have wide ranging application in both heterogeneous and homogeneous catalysis. Recent environmental and economic problems offer a challenge for developing new catalysts capable of deep hydrodesulfurization (HDS) and hydrogenation of aromatics in the presence of sulfur and nitrogen compounds. Unsupported ruthenium sulfides were reported to show a high activity for HDS and hydrogenation (1,2). The catalytic activity for HDS reaction is likely to depend upon greatly the preparation and pretreatment of the ruthenium catalysts, such as surface composition, surface acidity, and electronic property of ruthenium (3,4). The objective of this study was to report the effects of catalyst pretreatment on the catalytic activity of an alumina-supported ruthenium catalyst for thiophene HDS.

EXPERIMENTAL

0.49% $\text{Ru}/\text{Al}_2\text{O}_3$ (JRC-A4-0.5Ru2) was prepared by impregnation of alumina powder with aqueous solution of ruthenium trichloride. 0.2 g of catalyst was charged to the reactor for a typical series of experiments. The $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst was pretreated with three ways prior to catalyst characterization and activity measurement; reduced in H_2 for 4 h (Ru-R catalyst), oxidized in air at 400 °C for 3 h, following reduction in H_2 for 4 h (Ru-OR catalyst), or sulfided in a 10 % $\text{H}_2\text{S}/\text{H}_2$ stream (Ru-S catalyst). The HDS activity measurement for thiophene HDS was carried out in a continuous-flow microreactor.

The surface property of the catalyst was measured by NH_3 -TPD, H_2 adsorption, XPS, and in-situ DRIFT FT-IR spectroscopy. For the NH_3 -TPD experiment, the catalyst was heated to 500 °C at a rate of 10 °C/min under He flow. It was maintained under these conditions for 1 h and then slowly cooled to room temperature. The He flow was switched to a 5.1% NH_3/He flow to adsorb NH_3 to the catalyst. The catalyst was heated at a rate of 10 °C/min to 500 °C (or 600 °C) under He flow. The outlet gas was analyzed by either a gas chromatograph or a quadrupole mass spectrometer with a valunerable-leak valve. Hydrogen adsorption was analyzed by a thermal conductive detector of a gas chromatograph after the pretreatment. The H_2 uptake was measured using pulses of 10 % H_2/He to the reactor at room temperature. The surface composition of the catalyst was measured by X-ray photoelectron spectroscopy.

RESULTS AND DISCUSSION

The physical properties and HDS activity of the catalyst are shown in Table 1. The Ru-S300 catalyst was the most active of the all catalysts for thiophene HDS, but the Ru-S400 catalyst had lowest activity. The Ru-OR300 catalyst was more active than the Ru-R200 and Ru-R400 catalysts.

Three kinds of peaks (low-, middle-, and high-temperature) were observed in NH_3 -TPD profile. The Ru-S300 and Ru-OR300 catalysts have a predominant high-temperature peak with a small low-temperature peak. However, the Ru-S400, Ru-R200 and Ru-R400 catalysts have no high-temperature peaks, but middle-temperature peaks together with a small low-temperature peak. Alumina support has only middle-temperature peaks in the NH_3 -TPD profile. Mass spectroscopy and XPS analyses showed that the low-, middle- and high-temperature peaks were assigned to RuO_2 (280.7-281.1 eV), acid sites on alumina, and Ru metal (280.2 eV),

respectively (5,6). The spectra at 280.2 eV was not observed for the fresh catalyst but for the reduced and sulfided catalysts.

The HDS activity was not concerned with low-temperature peak of NH_3 -TPD, but high-temperature peak. The high-temperature peak of NH_3 -TPD was related to H_2 adsorption and the intensity of XPS Ru3d spectra at 280.3 eV (Ru metal).

The particle size was determined by H_2 chemisorption at room temperature. The Ru-R300 catalyst had smaller particles than the Ru-R400 catalyst. The selectivity of the Ru/ Al_2O_3 catalyst for hydrogenation of butenes to butane in thiophene HDS was calculated. The ratio of butane/butenes indicated the hydrogenation activity. The ratio for the Ru-R400 catalyst was higher than that for the Ru-R300 catalyst. The ratio of butane/butenes in the products was increased with increasing particle size for the catalyst. The selectivity of the Ru-R400 catalyst was more than the Ru-R300 catalyst for the hydrogenation of butenes to butane. Since the particle size of the Ru-R400 catalyst was larger than that of the Ru-R300, the large Ru particle of the catalyst appeared to facilitate the hydrogenation of butenes to butane. The particle size was concerned with the selectivity of butane/butenes (hydrogenation) in the reaction.

LITERATURE CITED

- (1) Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67** 430 (1981).
- (2) Lacroix, M., Boutarfa, N., Guillard, C., Vrinat, M., and Breysse, M., *J. Catal.* **120**, 473 (1989).
- (3) Cocco, A., and Tatarchuk, B. J., *Langmuir* **2**, 1309 (1989).
- (4) Lu, K., and Tatarchuk, B. J., *J. Catal.* **106**, 166 (1987).
- (5) De los Reyes, J. A., Gobilos, S., Vrinat, M., and Breysse, M., Grimblot, J., *J. Catal.* **142**, 455 (1993).
- (6) Mitchell, P. C. H., Scott, C. E., Bonnelle, J.-P., Grimblot, J. G., *J. Catal.* **107**, 482 (1987).

Table 1. Surface property and HDS activity of Ru/ Al_2O_3 Catalyst

Catalyst	Pretreatment Temp.			Conversion [%]	Amount of adsorbed H_2 [10^{-2} ml/g]	Ru particle size [nm]	NH_3 -TPD ⁴⁾		
	Oxi ¹⁾	Red ²⁾	Sul ³⁾				LTP	MTP	HTP
							[°C]		
Ru-OR300	400	300	-	37.5	6.8	2.6	167s	327m	427s
Ru-OR400	400	400	-	14.6	2.2	7.6	192s	321m	
Ru-R300	-	300	-	51.5	1.2	4.5	200w	300m	
Ru-R400	-	400	-	8.8	1.0	22.9	200w	300m	
Ru-S300	-	-	300	13.9	8.9	2.0	178s	364m	418s
Ru-S400	-	-	400	4.9	0.8	26.6	186w	330w	

1)Oxidation, 2)Reduction, 3)Sulfidation, 4)LTP, MTP, HTP, and w, m and s represent low-, middle-, and high-temperature peak, and weak, middle and strong intensity, respectively.

EVIDENCE FOR THE TRIBOCHEMICAL GENERATION OF HYDROGEN FROM HIGHER RANK COALS

Karl S. Vorres
Chemistry Division, Bldg. 211
Argonne National Laboratory
Argonne, IL 60439

ABSTRACT:

Analysis of gases in sealed ampoules of higher rank Argonne Premium Coal Samples over a period of years has revealed the presence of significant (up to about 18%) constant amounts of hydrogen and increasing amounts of carbon dioxide. Comparison with the gas contents of sealed 55 gallon drums which have not been pulverized indicates that these gases came from activity following the collection of the samples. Several hypotheses are examined. The evidence indicates a possible tribochemical reaction involving fresh surface generated during pulverizing in the nitrogen atmosphere. It is probable that water reacts with the coal surface to release hydrogen. The oxygen from the water appears to bound to active sites, and later diffusion leads to formation and release of carbon dioxide.

INTRODUCTION:

The Argonne Premium Coal Sample Program (1) has produced a set of coal samples which have been sealed in glass for periods of up to 9 years. As part of a study of the stability of these samples, analyses of the gas in the ampoules have been made at varying intervals. The original objective of studying the oxygen concentration was readily met, and the analytical data provided additional insights into interesting changes during the storage period and also in the processing of the coal itself.

It has been observed (2) that a number of gases have accumulated. Not surprisingly, the lower rank coals release carbon dioxide and the higher rank coals evolve methane. It has also been observed that substantial amounts of hydrogen have been found in the samples of some of the higher rank coals. In addition increasing amounts of carbon dioxide were observed in some of the higher rank coals.

A number of hypotheses were formulated and tested to account for these observations. This paper describes the hypotheses and efforts to understand these observations.

EXPERIMENTAL

The collection of the Premium Coal Samples was done with very fresh samples which were transferred to 55 gallon stainless steel drums. These drums were taken to the surface of the underground mines, and purged with argon gas within .5-5 hours of the collection. Purging continued to give about 100 ppm or less of oxygen in the drums, with an overpressure of a few psi. After 1-2 days of travel to the Argonne National Laboratory, the drums were processed in a large (2000 ft³) glove box containing a crusher, pulverizer, mixer-blender and packaging equipment. This glove box was filled with nitrogen and kept at or below 100 ppm oxygen during the processing.

For a typical processing, the coal was initially crushed to pass between bars spaced at .5", pulverized to -20 mesh, and blended in a one ton batch. Half a ton of -20 mesh coal was packed in 5 gallon leverlock pails, moved through air locks and repulverized to -100 mesh. About 80% of the coal was placed in 5 gallon glass carboys, while the balance was sealed in ampoules containing either 5 grams of -100 mesh or 10 grams of -20 mesh material. The sealing was done with a torch using stoichiometric hydrogen and oxygen, controlled with a mass flow controller.

At all processing times, the gas contents in the glove box were monitored by an oxygen analyzer, hydrogen analyzer and total hydrocarbon analyzer (Beckman model 108A). Sample lines led from central points in the box, air locks, and other critical locations in the system to the analyzing system.

The oxygen concentration in the box was controlled during the operation by circulating the atmosphere through ductwork connecting the boxes to a catalytic reactor containing palladium-on-alumina catalyst. The reactor was connected to a supply of hydrogen which permitted the impurity oxygen to combine to produce steam. Upstream from the catalytic reactor were a high efficiency particulate filter with pressure differential measuring equipment and a cyclone separator for larger particulate material.

In operation the hydrogen concentration in the box was to be kept below 1.0%. The gauge had a single range with a maximum reading of 5%.

A typical sample consisted of one ton of coal held in six drums. A seventh drum was collected and retained for archival purposes. The gas pressure in the drums increased substantially for some samples and periodically required release of some gas for safety.

RESULTS AND DISCUSSION

Gas analyses were run by the Analytical Chemistry Laboratory at ANL and reported in volume percent. A set of ampules was provided which were opened in an evacuable chamber in a CEC mass spectrometer, and more recently in a VG 3001 mass spectrometer.

The data were reported for the species which were observed by the analyst. These species were: nitrogen, argon, water vapor, methane, carbon dioxide, ethane and higher hydrocarbons and hydrogen. The use of the VG spectrometer permitted resolution of the nitrogen and carbon monoxide in more recent measurements. Recently ammonia was also observed and other samples were checked for this gas.

In general the concentrations of a gas are higher in the -20 mesh ampules than the -100 mesh containers. The gas volume per gram of coal is comparable for most samples. The exception to this generalization is hydrogen. For hydrogen, the concentrations are higher in the -100 mesh ampules. This observation is consistent with a process-related origin for the majority of this gas.

The results obtained for the carbon dioxide analyses (six highest concentrations) are indicated in Figure 1.

The results for the hydrogen analyses are shown in Figure 2.

The operating records for the processing were checked for appearance of hydrogen in the process gas analysis system. In all cases with substantial release of hydrogen, the monitor indicated a rapid increase at the time the pulverizing started. The hydrogen supply to the catalytic reactor was checked, found to be normal, and shut off to prevent additional hydrogen entering the system from the gas cylinder.

Several hypotheses to explain the rapid appearance of the hydrogen and the slower appearance of the carbon dioxide were developed. Discussions with a number of individuals led to more. A summary of them follows, together with comments in support and against them.

Hypothesis 1: "The hydrogen and carbon dioxide were in the higher rank coal. The hydrogen was released more quickly because of its lower molecular weight."

Comments on hypothesis 1: The gases in the archival drums were sampled and analyzed. Hydrogen was below the limits of detection (.015%) while the hydrogen from the initial analysis of a -100 mesh Pocahontas ampule was 17.6%. Further, the carbon dioxide content of the gas in the drum of Pocahontas coal was 0.82%, while the methane was 52.9 and the ratio of the two was 0.016. The recent measurement of carbon dioxide in the -20 mesh sample gave 4.7% and the methane was 6.5% for a ratio of 0.72. Evidently much more carbon dioxide is evolved in the ampule than the drum.

Hypothesis 2: "The gases were produced by microbial action."

Comments on Hypothesis 2: Different workers have cultured samples. Some find no growth, while others find growth but only on low rank samples.

Hypothesis 3: "Coal dust found it way to the palladium catalyst, and lost hydrogen there."

Comments on hypothesis 3: The volume of the box is 2000 ft³. The hydrogen content from the Pocahontas sample was up to 14.7%. That represents almost one pound mole or about 2 pounds of hydrogen. Since the coal is about 4% hydrogen, the observed concentration would require the equivalent of about 40 pounds of coal accumulating on the catalyst bed and losing all of the hydrogen. Such a substantial deposition would require a major break in the filter and would have been observed in a notable drop in the pressure differential across the filter. That drop was not observed.

Hypothesis 4: "The methane gas coked on the palladium catalyst, releasing hydrogen". That may have been possible, however the catalyst activity did not decrease as might have been expected. The carbon dioxide generation is not explained by this hypothesis.

Hypothesis 5: "Low temperature oxidation produced the hydrogen as a byproduct."

Comments on hypothesis 5: Low temperature oxidation has been shown to produce hydrogen as a byproduct gas (5,6). The reported hydrogen gas concentrations range up to 1121 ppm for reaction with oxygen over 65 hours. The experiments showed about 11 ppm per 1% of oxygen consumed at 95°C. The hydrogen concentrations observed in the ampules from the processing facility ranged up to 17.6% (176,000 ppm) or two orders of magnitude greater than the maximum observed for the low temperature oxidation studies. The hydrogen production in the facility is a moderately rapid reaction during and after pulverizing. The oxygen consumption reported is much greater than the hydrogen production. In the processing facility the oxygen available was less than 100 ppm, while the hydrogen production was four orders of magnitude greater. The relative humidity in the processing facility was indicated to vary from 42 to 91%. A significant amount of moisture was available for reaction.

Hypothesis 6: "Tribochemical reactions are responsible for both of the gases."

Comments on hypothesis 6: Tribochemistry deals with the chemical reactions that are due to adding mechanical energy to a system (3). Pulverizing is an example. The surface of a solid is disturbed to a depth of about 10 atom layers in many solids during pulverizing. The disrupted zone is called the Beilby layer. The imperfections caused by grinding permit gases to readily diffuse through the damaged surface into the Beilby layer. During pulverizing fractures cleave bedding planes for the coal, but also break through the large macromolecular structure, rupturing carbon-carbon and other bonds. Radicals are created in this process. Water molecules are present from water contained in the coal and in the gas atmosphere. Through a succession of reactions, the water molecules could react with active sites on the fresh surface, and hydrogen could be removed while oxygen remained bound to the surface. The hydrogen could escape quickly, giving the rapid observed increase in hydrogen concentration. The slower increase of carbon dioxide could be attributed to a slow diffusion of oxygen around the surface until two oxygen atoms joined a removable carbon to form carbon dioxide.

CONCLUSIONS

The observation of an increasing hydrogen evolution with some higher rank coals during the processing of the large chunks into pulverized material has been made. Carbon dioxide has also been observed, but in smaller amounts. A number of hypotheses have been examined to explain this behavior. The most plausible at this time seems to be the tribochemical generation of hydrogen due to the creation of chemically active sites as a result of the

pulverizing. Reaction of moisture with the coal results in relatively rapid release of hydrogen and bonding of oxygen to the surface. A slow diffusion of oxygen around the surface coupled with release of gaseous carbon dioxide then follows. Additional work with isotope ratios for the carbon, hydrogen and oxygen species should help confirm the nature of the reactions and is planned.

ACKNOWLEDGMENTS

The author expresses appreciation to the Office of Basic Energy Science, Chemical Sciences Division, U. S. Department of Energy for support for this work.

REFERENCES

1. Vorres, K. S. *Energy Fuels* **1990** 4 420-
2. Vorres, K. S., *Proc. 7th Int. Conf. Coal Sci.* **1993** II 367-370; K. H. Michaelian, Ed. See also: Vorres, K. S., *Preprints, Fuel Chem. Div., Am. Chem. Soc.*, **1992** 37 (4) 1945-1950
3. Heinicke, G. "Tribochemistry" Carl Hanser, Berlin, 1984
4. Polman, J. Kevin; Breckenridge, Cynthia R.; Delezene-Briggs, Karen M., *Energy Fuels* **1993** 7 (3) 380-383
5. Grossman, S. L., Davidi, S., Cohen, H. *Fuel* **1991** 70:7 897-8
6. Grossman, S. L., Davidi, S., Cohen, H. *Fuel* **1993** 72:2 193-7

Fig. 1, Six Highest -20 Mesh Carbon Dioxide Concentrations

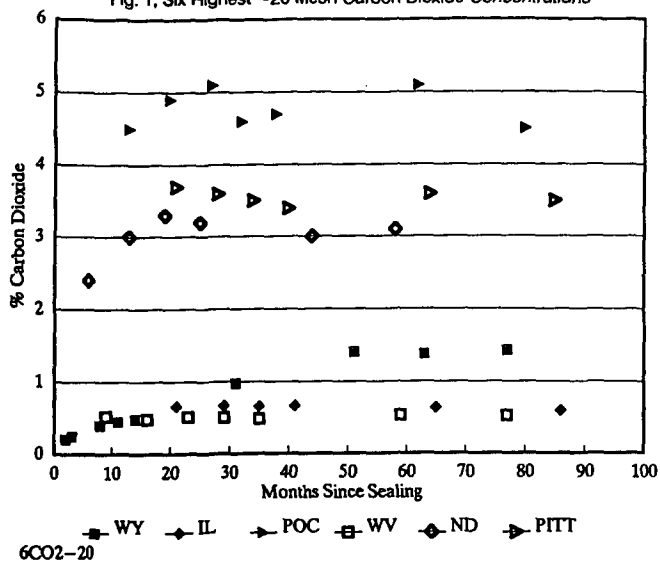
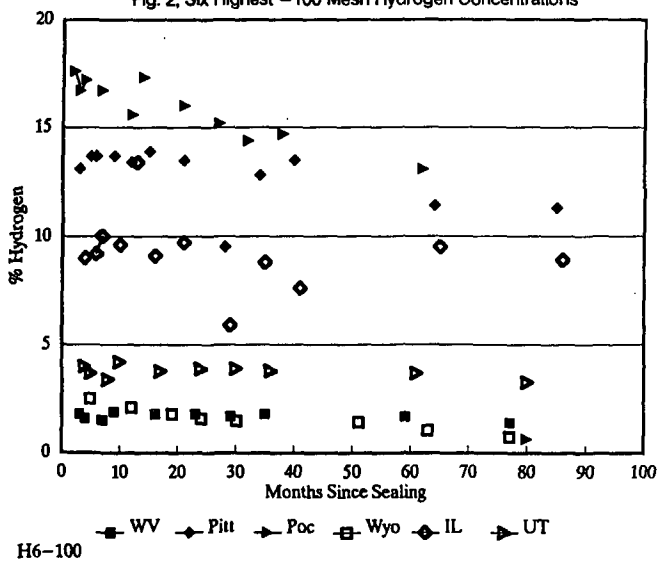


Fig. 2, Six Highest -100 Mesh Hydrogen Concentrations



BIOMIMETIC SOLUBILIZATION OF BROWN COAL BY OXYGENASE MODEL WITH HYDROGEN PEROXIDE

Keiji Miki and Yoshiaki Sato
Energy Resources Department
National Institute for Resources and Environment
16-3, Onogawa, Tsukuba, Ibaraki 305
Japan

Keywords: Brown coal, Solubilization, Oxygenase model

INTRODUCTION

As an alternative processing of coal conversion, biosolubilization has been intensively studied[1-4]. Most of the studies in 1980's involve the oxidative solubilization of preoxidized coal or lignite to render the coal water soluble. The products contain primarily polycarboxylic compounds and are suggested to be of lower quality than the materials derived from conventional thermochemical conversion[5]. Thus there has been arguments about the biological processes for the production of alternate fuels or chemicals from coal[6]. Current reductive solubilization of coal under anaerobic conditions could provide more desirable products[7,8]. On the other hand, these biological processes imply a potential route to liquefy coal catalytically under considerably mild conditions. The elucidation of mechanisms involved in the biosolubilization and the application of the catalyst systems in analogous to enzymes or microorganisms may offer an attractive processing for coal conversion.

During the past decade, numerous studies on oxidation reaction catalyzed by synthetic metalloporphyrin have been reported[9]. These catalysts have been synthesized as the models for cytochrome p450 and peroxidase, and some of them exhibit extremely high turn over number in the oxidations of alkenes and alkanes[10,11]. To date the mechanisms of oxidation reactions catalyzed by synthetic metalloporphyrins are fairly well understood and the utilization of the catalyst for the oxidations of various stable compounds is of great interest. Preliminary attempt using a simple iron porphyrin complex for coal conversion, however, did not show a significant effect on the solubilization. In addition, the contamination of catalyst and residual oxidant affected the evaluation of the products. Therefore as the first step, we developed a new supported biomimetic catalyst capable of using hydrogen peroxide as an oxidant. In this paper we describe the solubilization of coal by the oxygenase model, immobilized iron porphyrin catalyst.

EXPERIMENTAL

Preparation of catalyst

A biomimetic model for monooxygenase enzyme was synthesized on a silica surface as the following 5 steps (Fig. 1), based on the detailed design considering the structures of bulky porphyrin and the silica surface[12]. 1) Amorphous silica powder, Aerosil 200, was dispersed in toluene to which 3-mercaptopropyltrimethoxysilane was added. Refluxing overnight and removal of solvent under vacuum yielded the support-anchored silica (a). 2) A was dispersed in pyridine, to which phthalocyaninatoiron (II) was added. The mixture was stirred overnight and the solid collected by filtration. Drying under vacuum gave phthalocyaninatoiron-loaded silica (b). 3) B was dispersed in CH_2Cl_2 , to which excess dodecyltriethoxysilane was added. After removing solvent, the container was evacuated, sealed and heated for 24 h at 150-160°C. It was cooled, opened and washed with CH_2Cl_2 and acetone resulting hydrophobic silica (c). 4) C was subjected to Soxhlet extraction with pyridine for 72 h and yielded iron-free silica (d). 5) D was dispersed in benzene, to which iron tetraphenylporphyrin acetate was added under argon. After refluxing 48 h with stirring, the solid was collected by filtration and washed with CH_2Cl_2 until the filtrate turn to colorless. The dark green solid obtained (E) had a loading of iron tetraphenylporphyrin complex of $1.34 \times 10^{-2} \text{ mmol g}^{-1}$.

Solubilization of brown coal

A brown coal (Australian Yallourn coal), ground to $<149 \mu\text{m}$, dried and stored in a glass ampoule, was used.

The catalyst ($1.0\text{--}1.5 \mu\text{mol}$) and the coal (300 mg) were dispersed in 10 ml of deionized water or acetate buffer (pH 5.0) to which imidazole (1 mmol) and H_2O_2 (2 mmol) were added. The container was sealed with a septum and shaken at 150 stroke/min at 40°C using a Bio-shaker for 24 h. For anaerobic assays, manipulations were done in a glove box.

After reaction, the mixture was filtrated and extracted with tetrahydrofuran/H₂O (v/v=4:1) until the filtrate turn to colorless. The filtrate and extract were combined, evaporated and dried at 110°C under vacuum.

RESULTS AND DISCUSSION

Catalytic activity of oxygenase model

As mentioned above, from the point of product quality, it is most desirable to mimic enzymes functioning reductive reactions under anaerobic conditions. But the studies on such enzymes involving electron transfer seem to be at an early stage. For that reason we attempted the synthesis of the model for cytochrome P450 monooxygenase.

The active sites, iron tetraphenylporphyrin units, were immobilized by coordinative ligation to anchored mercaptopropyl groups in hydrophobic cavities formed by alkyl chains attached to silica surface. This is the characteristic structure distinguished from other efficient iron porphyrin catalysts (Table 1). When the oxidation reaction is performed in aqueous solution, lipophilic substrates are assumed to condense on the catalyst surface by hydrophobic interactions. Further it inhibits contact between the active center and H₂O₂. As the result, the catalytic reaction takes place even with a small amount of substrate without the decomposition of fragile porphyrin structure by H₂O₂ attack.

The catalytic activity of the synthetic catalyst was clarified by the epoxidation of alkenes. In the presence of externally added imidazole, the substrates were efficiently epoxidized (Table 2). Although the iron center have an axial sulfur ligand in the same manner as native enzyme, the promotion of heterolytic cleavage of H₂O₂ by general catalyst seems to be required. Thus the following coal solubilization reactions were carried out in the presence of imidazole.

Solubilization of brown coal

It has been reported that coal reacts rapidly with H₂O₂ in the study on the coal solubilizing activity of horseradish peroxidase[13]. H₂O₂ is known to decompose at a higher pH, but a lower pH may favor hydrolysis reaction of coal. Further the aqueous buffers contaminate the residue in the concentrated solubles. Hence controls were always run and deionized water was mainly used in the coal solubilization experiments. As shown in Table 3, a considerable amount of soluble fraction was obtained after the treatment with H₂O₂ or H₂O₂/imidazole in the absence of the catalyst. The yields seem to be strongly affected by the presence of oxygen and imidazole.

The results indicate clearly the effect of catalyst addition in every series of experiments. The presence of 1 μmol catalyst increased in conversion by 10-15% under aerobic conditions. Anaerobic assay required a slightly larger amount of catalyst to obtain the similar conversion. No appreciable effect on the solubilization was found in the absence of imidazole.

Elemental analyses showed high nitrogen contents in the products derived from imidazole-added runs. There was a difficulty in removing it completely even by prolonged vacuum drying at 110°C. Therefore the correction of elemental compositions was made for the evaluation of oxygen incorporation. The amount of imidazole in the product was calculated from the excess of nitrogen, assuming that the nitrogen content equals that in imidazole-free control. The results showed the remains corresponding to about a half of initially added imidazole. Recalculated elemental compositions from the data were shown in Table 4. The catalytic treatment caused a decrease in carbon content and an increase in oxygen content. The change is not so drastic as seen in the oxidative microbial conversion. As the result, the solubilization reaction does not involve the introduction of a high concentration of carboxylic acid. The assumption is also supported by FT-IR analysis which reveals the decrease in the relative intensity of carbonyl band to aromatic band by the catalyst addition compared with that from control. Further no aromatic acid derivative is detected in the catalytic oxidations of various model compounds.

At present further detailed studies are in progress to explore the function of biomimetic model in connection with the solubilization reaction of coal, including the capability of catalytic carbon-carbon bond scission.

CONCLUSION

A biomimetic model for monooxygenase enzyme was synthesized and utilized for the solubilization of brown coal. In the presence of imidazole as a general catalyst and H₂O₂ as an oxidant, it was suggested that the model catalyzed the solubilization reaction of coal. This is partly due to the characteristic nature of the model in addition to the catalytic activity.

REFERENCES

1. Cohen, M.S., and Gabriele, P.D., *Appl. Environ. Microbiol.*, **1982**, 44, 23-27
2. Couch, G.R., "*Biotechnology and Coal*", **1987**, IEA Coal Research, London
3. Cohen, M.S., Bowers, W.C., Aronson, H., and Gray, Jr., E.T., *Appl. Environ. Microbiol.*, **1987**, 53, 2840-2843
4. Pyne, Jr., J.W., Stewart, D.L., Fredrickson, J., and Wilson, B.W., *Appl. Environ. Microbiol.*, **1987**, 53, 2844-2848
5. Wilson, B.W., Bean, R.M., Franz, J.A., and Thomas, B.L., *Energy & Fuels*, **1987**, 1, 80-84
6. Narayan, R., and Ho, N.Y., *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, **1988**, 33, 487-495
7. Jain, M. K., Burgdorf, D., and Narayan, R., *Fuel*, **1991**, 70, 573-576
8. Scott, C.D., Faison, B.D., Woodward, C.A., and Brunson, R.R., *1991 Second International Symposium on the Biological Processing of coal*, **1991**, EPRI, Palo Alto, CA, 4-5-4-22
9. Meunier, B., *Chem. Rev.*, **1992**, 92, 1411-1456
10. Traylor, P.S., Dolphin, D., and Traylor, T.G., *J. Chem. Soc., Chem. Commun.*, **1984**, 279-280
11. Traylor, T.G., Tsuchiya, S., Byun, Y-S., and Kim, C., *J. Am. Chem. Soc.*, **1993**, 115, 2775-2781
12. Miki, K., and Sato, Y., *Bull. Chem. Soc. Jpn.*, **1993**, 66, 2385-2390
13. Quigley, D.R., Breckenridge, C.R., Polman, J.K., and Dugan, P.R., *Fuel*, **1991**, 70, 581-583

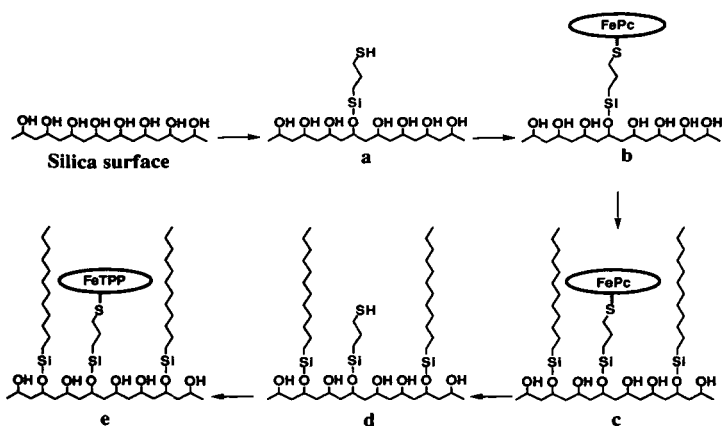


Fig. 1 Synthetic pathway of oxygenase model

Table 1. Structure and reaction system of oxygenase model and efficient iron porphyrin catalyst

active center	reaction site	axial ligand	oxidant	medium	reference
<u>oxygenase model</u>					
FeTPPOAc ^{a)}	highly hydrophobic	immobilized alkyl thiol	H ₂ O ₂	H ₂ O	this work
<u>efficient iron porphyrin catalyst</u>					
FeTDCPPCI ^{b)}	—	imidazole	H ₂ O ₂	CH ₂ Cl ₂ /CH ₃ CN	9
FeTDCPPCI	—	—	C ₆ H ₅ IO C ₆ F ₅ IO	CH ₂ Cl ₂ /MeOH	10
FeTPFPCCI ^{c)}	—	—	H ₂ O ₂	CH ₂ Cl ₂ /MeOH	11

a) Iron tetraphenylporphyrin acetate. b) Iron tetrakis(2,6-dichlorophenyl)porphyrin chloride. c) Iron tetrakis(pentafluorophenyl)porphyrin chloride.

Table 2. Oxidation of alkene with immobilized iron porphyrin and hydrogen peroxide^{a)}

run	atmosphere	substrate	product ^{b)}	
			oxide	aldehyde
1	aerobic	<i>trans</i> -β-methylstyrene	125	154
2	anaerobic	<i>trans</i> -β-methylstyrene	98	45
3	aerobic	<i>cis</i> -stilbene	30	7
4	anaerobic	<i>cis</i> -stilbene	31	5
5	aerobic	<i>cis</i> -cyclooctene	49	-
6	anaerobic	<i>cis</i> -cyclooctene	42	-

a) Alkene / H₂O₂ / imidazole / catalyst = 0.4 mmol / 0.4 mmol / 0.2 mmol / 4mmol in 2ml H₂O at 40° C for 17h. b) Yield based on equivalents of catalyst used.

Table 3. Solubilization of Yallourn coal with immobilized iron porphyrin and hydrogen peroxide^{a)}

run	catalyst (μmol)	imidazole (mmol)	H ₂ O ₂ (mmol)	conversion (%)
1-1	0	0	2	51
1-2	0	1	2	23
1-3	1.0	1	2	66
2 ^{b)} -1	0	0	2	26
2-2	0	1	2	41
2-3	1.0	1	2	44
2-4	1.5	1	2	53
3 ^{c)} -1	0	0	2	44
3-2	0	1	2	46
3-3	1.0	1	2	56

a) Yallourn coal (300mg) was treated in deionized water (10ml) at 40°C for 24 h. b) Under argon.
c) In 200 mM acetate buffer at pH 5.0.

Table 4. Elemental analysis of solubilization product^{a)}

run	elemental analysis					
	C	H	N	O+S	H/C	O/C
		(%)				
original coal	64.2	4.9	0.7	30.2	0.91	0.35
1-1 ^{b)}	59.7	4.9	1.1	34.4	0.97	0.43
1-2	59.4	4.6	1.1	35.0	0.93	0.44
1-3	60.0	4.5	1.1	34.4	0.90	0.43
2-1	59.9	5.0	1.2	34.0	1.00	0.43
2-2	60.0	4.7	1.2	34.2	0.93	0.43
2-3	60.2	4.6	1.2	34.2	0.91	0.43
2-4	60.3	4.6	1.2	34.0	0.92	0.42

a) Corrected data (Refer to text). b) Run number is the same in Table 2.

OXIDATIVE DESULFURIZATION OF LIQUID FUELS

Tetsuo Aida*, Daichi Yamamoto

Department of Industrial Chemistry, Faculty of Engineering in Kyushu
Kinki University
11-6 Kayanomori, Iizuka, Fukuoka 820, JAPAN

Keywords: Desulfurization, Liquid fuels, Oxidation reaction

INTRODUCTION

Among the alternatives of petroleum oil, coal is considered to be one of the most practical energy resources in the next generation, because of its unlocalized abundance. Under such circumstances, the consumption of the fossile fuel such as petroleum oil or coal-derived liquid fuels could be drastically increased in the next decade, and it will take place fatal environmental problems like an acid rain and a global warming. Particularly, the increase of the emission of sulfur oxides due to a combustion of those fuels is seriously concerned in the developing countries. Although it has long been anticipated the development of efficient desulfurization technologies for fossile fuels, except the flue-gas desulfurization processes, most of the research projects seem to be in trouble. In particular, the desulfurization of diesel fuels such as light or heavy oils is going to be critically important to sustaine our modernized life.

we had initiated research projects for developing efficient chemical desulfurization processes of coal, and revealed that the oxidation reaction significantly enhanced the chemical reactivity of the organic sulfur fuctionalities in coal, and it made them easy to remove from a solid coal. For instance, the alkaline fusion under oxygen gas, "Oxy-Alkalinolysis", achieved the sulfur removal upto 95-98% for most of the coals(1). To use such drastic change of the chemical and phisical properties of organic sulfur compounds by oxidation is our strategy for developing an efficient desulfurization process for liquid fuels.

This paper present the results of the study on the desulfurization process using oxidation reactions for liquid fuels.

PROPOSED PRINCIPLE OF OXY-DESULFIRIZATION POR LIQUID FUELS

In general, there are many types of organic sulfur compounds in the fossile fuels. In particular, arylic sulfide-type sulfur and thiophene-type sulfur such as , benzothiophene or dibenzothiophene are believed to be major components(2). These types of organic sulfur atom are known to be chemically so stable that the carbon-sulfur bond-fission does not occur easily. Traditionally, the catalytic hydrogenetaion reaction has been used for such bond cleavage, which has several advantages for industrial purposes, but also some disadvantages. Particularly, the use of hydrogen gas and catalyst forced to take more and more drastic reaction conditions(higher pressure and higher temperature) in order to get the higher degree of the sulfur removal. In Japan, it is assumed that the cost of the capital investment to decrease the sulfur content in a commercial light upto 0.05%-level will be over five hundred billion yen(3). The recent researchs revealed that one of the reason of the difficulty of sulfur removal from a light oil will be the steric hindrance due to the alkyl functions surrounding the sulfur atom in the sulfur compounds. This means that the developement of highly active catalysts may be vital to achieve the long term target , but there seems to be a fatal limitation.

In the meantime, the principle of the proposed oxydative desulfurization process is as follows: It may be very fortunate for us that the most of the organic sulfur atoms in the fossile fuel are thought to be divalent, like a sulfide or thiophene. In general, oxidized sulfur compounds such as sulfoxide or sulfone have

significantly different chemical and physical properties, particularly boiling point and solubility towards various solvents based on a molecular polarity, compared to the corresponding divalent compounds.

Now, an simple idea comes in our mind, that is, a large degree of differences of the boiling point and polarity before and after oxidation should make easy to separate them from other hydrocarbon components through ordinary purification procedures like a distillation, an solvent extraction or/and a chromatographic adsorption.

It can be also emphasized that this process could provide the organic sulfur components in the fuels as a potential low materials to the industrial uses. Namely, our understanding is that the sulfur components in fossil fuels is not a waste. It is a valuable natural resource.

EXPERIMENTAL

Solvents and Reagents: Gold label grade reagents were used without further purification.

Sulfur Analyses: High sensitivity sulfur analyzer(Model TS-03, Mitsubishi Kasei Co.) is used for the determination of sulfur content in the liquid fuels.

Oxidation of Liquid Fuels: A typical run as follows. In the three necked flask(300ml) equipped by a mechanical stirrer and reflux condenser, 100ml of liquid fuel was placed, and a mixture of formic acid(10ml) and aqueous hydrogen peroxide (30%, 10ml) was added with vigorous stirring keeping temperature below 60°C for 2 hours. After the reaction the reaction mixture was cooled down at ice-water temperature, and separated the oil layer, and washed by distilled water.

Solvent Extraction: Extraction of sulfur components was carried out by using same amount of liquid fuel and extraction solvent (1/1 vol/vol).

Adsorption: Adsorption of sulfur component in liquid fuel was carried out by using a column chromatography packed by absorbent(silica gel or alumina). The ratio of the liquid fuel and absorbent was 100/10(wt). The sulfur content was determined to the combined liquid passed through the column.

RESULTS AND DISCUSSION

Obviously, the key step of this desulfurization process is the oxidation reaction, which has to selectively oxidize the sulfur atom in the contamination. We have examined many type of oxidants, and found that the peroxyacid, like a performic acid or a pertrifluoro acetic acid, was one of the positive candidate for that. These oxidants are known to oxidize not only sulfur compounds but also olefinic hydrocarbons affording the corresponding epoxy compounds. However, we do not think that this type of the side reaction causes critical damages to the total fuel efficiency.

The reaction mechanism of the oxidation of organic sulfur compound, i.e., dibenzothiophene, by performic acid(a mixture of formic acid and hydrogen peroxide) is illustrated as shown in Figure 1. Namely, formic acid reacts with hydrogen peroxide and gives performic acid and water. Then, the performic acid reacts with dibenzothiophene and gives dibenzothiophene sulfoxide, and a further oxidation gives the corresponding sulfone. Thus overall oxidation reaction consumes only hydrogen peroxide recycling formic acid.

We have initiated this research project from a modeling experiments as follows: A model liquid fuel was prepared by using dibenzothiophene as organic sulfur and cyclohexane as hydrocarbon component. The sulfur content in the model fuel was controlled in 0.30% and it was treated by the mixture of formic acid and aqueous hydrogen peroxide(30%) below 60°C temperature for 2 hours. After the reaction, the mixture was cooled down at 0°C, and resulted white

crystal was filtrated which was determined as dibenzothiophene sulfone. The sulfur content of the filtrate was 0.002%. Then the filtrate was extracted by aqueous dimethylformamide(water content, 3%). The cyclohexane layer was separates an washed with distilled water. After dried over anhydrous magnesium sulfate, the sulfur content was determined as 0.0007%. Also, the filtrate was passed through a silica gel column(oil/silica gel = 100/10 wt/wt). The sulfur content of the eluted solution was 0.0000%(exceeded the detectable limit of the sulfur analyzer Model TS-03, Mitubisikasei Co.)

Based on the results described above, the working principl seems to be correct. It will be also true that the sulfur comonents in liquid fuel such as light oil is not simple like in this model. So that we have applied these procedures to the actual commercial light oil. Figure 2 shows the gas-chromatogram(OV-1, packed glass-column; FPD-detector) of the reaction mixture of dibenzothiophene by this oxidation system. The shift of the retention time of the reaction product(sulfone) clearly suggests the increased boiling point and polarity by oxidation.

Figure 3 shows the gas-chromatogram(OV-1, packed glass-column; FPD-detector) of the reaction mixture of a commercial light oil(sulfur content, 0.56%) before and after oxidation. The wide range of distribution of peaks is observed due to a mixture of alkylderivatives of mainly benzothiophene and dibenzothiophene. Interestingly, there is a significant deference between the retention time in both peak distributions before and after oxidation, which is considered to be resulted by the oxidation as well as shown in Figure 2

Table 1 and 2 show the part of the results examined the sulfur removals of the commercial light oil and its oxidized one, which were achieved by the solvent extraction and the adsorption by silicagel and alumina column-chromatography.

Table 1 Sulfur Removal of Light Oil by Solvent Extraction^{a)}

Solvent	sulfur content(%)	
	commercial light oil ^{b)}	oxidized light oil
Acetonitrile	0.52	0.057 (0.012)*
OMFC ^{c)}	0.49	0.018 (0.003)*

* Trifluoroacetic acid / hydrogen peroxide

a) Ratio of oil and solvent was 1 / 1(vol) and a single extraction

b) Original sulfur content was 0.56%

c) N,N-Dimethylformamide

Table 2 Sulfur Removal of Light Oil by Adsorption^{a)}

Adsorbent	sulfur content(%)	
	commercial light oil ^{b)}	oxidized & extracted(DMF) light oil ^{c)}
Silicagel	0.54	0.0046 (0.0009)*
Alumina	0.53	0.0038 (0.0005)*

* Trifluoroacetic acid / hydrogen peroxide

a) Ratio of oil and adsorbent was 100 / 5(wt) , glass column(ϕ =0.5mm)

b) Original sulfur content was 0.56%

c) After extracted by N,N-Dimethylformamide

CONCLUSION

The proposed "Oxy-desulfurization Process" has exhibited a powerful ability to remove sulfur from diesel fuels like a light oil. The characteristic features of this efficient new process can be summarized as follows.

1. High degree of sulfur removal: Possible to down to a ppm-order sulfur-content
2. Mild reaction conditions: Ambient pressure and temperature
3. Useful by-product: Organic sulfur compounds
4. Applicable to heavier oil desulfurization
5. Economical ?

REFERENCE

* Author to whom correspondence should be addressed.

- (1) T. Aida, K. Ofuji, M. Fujii, M. Yoshihara, T. Yonezawa, T. Maeshima, Proc. Fukuoka International Sympo. Global Environment & Energy Issues, Fukuoka, JAPAN p.255(1990)
- (2) G. N. Georg and M. L. Gorbaty, J. Am. Chem. Soc., **111**, 3182(1977)
- (3) A. Inoue, Abstract Japanese Chemical Society National Meeting, Osaka, JAPAN p.2237(1992)

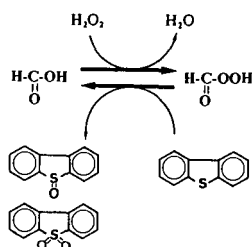


Figure 1 Oxidation reaction mechanism

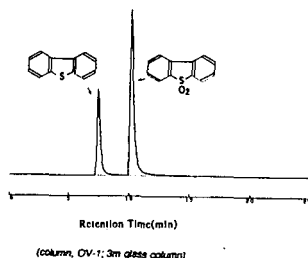


Figure 2. FPD-Gas chromatogram of Model-fuel oxidized by Formic acid/Hydrogen peroxide

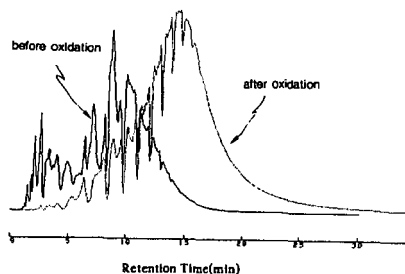


Figure 3 FPD-Chromatogram of Light Oil oxidized by Formic acid/Hydrogen peroxide